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THE DISPLACEMENT LAW OF ARC AND SPARK SPECTRA*

By W. F. Meggers, C. C. Kiess and F. M. Walters, Jr.

I. Introduction

About thirty years ago, when the structures of only the simpler arc spectra, principally those of elements in the first two columns of the periodic table, were known, it appeared that a general rule might be formulated to the effect that chemical elements of odd valency emit doublet systems while those of even valency have triplet systems.[1] The discovery of doublets in the spectra of the alkaline earths seemed to violate this rule, but in 1914 these systems were recognized as spark spectra and a relation between the line structure of a spectrum and the position of the element in the periodic table was reestablished. This relation was clearly expressed in 1919 by the *displacement* and *alternation* laws of Kossel and Sommerfeld.[2] The displacement law states that the spark spectrum of every element resembles in structure the arc spectrum of the element preceding it in the periodic system. The alternation law applies to either arc or spark spectra and in its modernized form it states that even and odd (odd and even) structures characterize the arc (spark) spectra of alternate chemical elements which occupy columns I to VIII of the periodic system.

In general, the experimental arc and spark spectra of any particular element contain many lines in common, that is, true spark spectrum

* Published by permission of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Kayser, Handbuch der Spectroscopie, II, p. 559.

[2] Kossel and Sommerfeld, Verh. Deutschen Physik. Ges. *19*, p. 241; 1919. Also Sommerfeld —Atombau und Spektrallinien, 3rd ed., p. 456; 1922.

lines are often excited in an ordinary electric arc while true arc lines always appear in high potential sources designed to develop characteristic spark lines. Theoretically, however, the two types of pure spectra are quite distinct, arc lines being emitted by excited neutral atoms, while the spark lines arise from energy changes in excited atoms which have lost one valence electron each. On this basis, according to Sommerfeld, the displacement and alternation laws had their theoretical origin in the conception that elements of each column of the periodic system are characterized by a certain valency which is ascribed to a certain number of *outer electrons* and this number progresses one unit at a time from left to right across the eight columns of the table in which the system of chemical elements is arranged. If now an atom loses one of its valence electrons by ionization, it is in effect displaced into the preceding column in which the number of outer electrons for normal atoms is one unit less. Thus the atoms normally classified in a given column will, when ionized, emit spark spectra resembling the arc spectra characterizing neutral atoms of the column adjacent on the left.

Although the validity of these laws has never been seriously questioned, the experimental verification, until recently, was confined to the first three columns since scarcely any spectral regularities were known except for the relatively simple spectra of elements in these groups. The work of Bohr, of Sommerfeld, and of Landé, has inspired spectroscopists to attack more complex spectra, and in rapid succession one spectrum after another has yielded to systematic and logical analysis the secret of its structure. Our attention was first given to the elements with atomic numbers 19 to 26 which occupy the fourth row of the periodic system I to VIII, viz., potassium, calcium, scandium, titanium, vanadium, chromium, manganese and iron. The empirical verification of the alternation law for the arc spectra of these elements extending across the entire table was announced just one year ago.[3] At the same time it was stated that investigations of spark spectra had been undertaken at the Bureau of Standards in order that the displacement law might be tested with the same elements which had verified the alternation law for arc spectra. The principal features of the spark spectra of all these elements are now known and the purpose of this paper is to present some of the evidence which proves the displacement law of Kossel and Sommerfeld.

[3] Meggers, Jour. Wash. Acad. Sci. *13*, p. 317; 1923.

II. LAWS OF SPECTRAL STRUCTURES

A brief review of the empirical and theoretical laws[4] which have been found to govern the structures of practically all spectra will be given here because the data below are, almost without exception, in conformity with these rules, thus indicating the general validity of the latter for spark spectra as well as for arc spectra.

In the early work on spectral series, different sequences of spectral lines were named Sharp, Principal, Diffuse, and Fundamental series, the wave number for any classified line being represented by the difference of two of the spectral terms symbolized by the letters S, P, D, and F. This usage has become so familiar that it seems desirable to continue it for the sake of uniformity even though the letters may not in all cases carry the exact meaning of the words which they abbreviate. Other types of spectral terms which have been more recently discovered are conveniently represented by the letters G, H, I, etc.

For our purposes, the specification of any spectral term is contained in three quantum numbers, k, j, n, and a multiplicity number r. Values of the *azimuthal quantum number* $k = 1, 2, 3, 4, 5, 6, 7$ are associated respectively with the S, P, D, F, G, H, I types of spectral terms. The *inner quantum number* j probably expresses the magnetic moment of an atom, and when the spectral terms are complex, different values of j distinguish the various sub-terms in the group. The *total quantum number* n determines the position of any term in the sequence or series to which it belongs. Finally, the number r indicates the permanent or maximum multiplicity attained in any system of terms. It is convenient to denote any particular term with the letter corresponding to its azimuthal quantum number, with n as a coefficient, j as a subscript, and r as a superscript. Thus $1D_3^5$ would represent the middle sub-level ($j = 3$) in the first group ($n = 1$) of D terms ($k = 1$) in a quintet system ($r = 5$).

The following scheme shows the inner quantum numbers associated with the spectral terms belonging respectively to systems of odd and even permanent multiplicities.

	Singlet	*Triplet*	*Quintet*	*Septet*
S	0	1	2	3
P	1	012	123	234
D	2	123	01234	12345
F	3	234	12345	0123456
G	4	345	23456	1234567

[4] Sommerfeld, Atombau und Spektrallinien, 3rd ed., Chap. 6; 1922, supplemented by references 5, 6, 7.

	Doublet	*Quartet*	*Sextet*	*Octet*
S	1	2	3	4
P	12	123	234	345
D	23	1234	12345	23456
F	34	2345	123456	1234567
G	45	3456	234567	12345678

The combinations of spectral terms which give rise to observed spectral lines are governed by the following selection and exclusion rules for the quantum numbers. As originally stated the rule for azimuthal quantum numbers was that only those term combinations for which the azimuthal quantum number k changes by plus or minus one unit are associated with radiation. Exceptions in which $\Delta k = 0$ or $\Delta k = \pm 2$ were usually ascribed to the influence of external electric or magnetic fields. The recent progress in analysis, especially of the more complex spectra, has made it necessary to extend the rule for azimuthal quantum numbers and such extensions have already been proposed by Laporte[5] and by Russell.[6] The normal appearance in Ca, Ti, Ti^+, V, Cr, Mn, Fe, etc., of many combinations between terms of the same spectral type, (eg., *PP*, *DD*, *FF*, etc.) indicated that two sets of terms must be present. According to Laporte these sets may be differentiated so that terms of different sets combine when $\Delta k = 0$ but not when $\Delta k = \pm 1$, while for combinations of terms within a set the original rule ($\Delta k = \pm 1$, $\Delta k = 0$ excluded) is valid. According to Russell, the terms in complex spectra may be sharply divided into two sets (not identical with Laporte's sets) such that no two terms in the same set combine with one another while any term of one set combines with all terms in the other for which the azimuth quantum changes by 0 or ± 1 or ± 2. These alternative statements of the azimuthal quantum rule are formally equivalent if we add to Laporte's that $\Delta k = \pm 2$ is permissible in combinations of terms between sets as he divides them.

The inner quantum numbers j obey the rule that j may combine either with j, $j+1$, or $j-1$, with the exclusion of the first named combination when $j = 0$. No exceptions to this rule are definitely known to exist.

These combination rules give rise to singlet lines or to line structures called multiplets which characterize the various spectra. Each spectrum line exhibits a characteristic Zeeman resolution in a magnetic field for which Landé[7] has given the comprehensive and exact scheme. The

[5] Laporte, ZS. für Physik, *23*, p. 166; 1924.
[6] Russell, Science, *59*, p. 512; 1924.
[7] Landé, ZS. für Physik, *15*, p. 189; 1923.

multiplet structures are further governed by rules relating to the relative intensities of the lines and to the wave-number intervals between the sublevels of the combining spectral terms. The intensity rule states that among the three possible transitions of j, the strongest line arises from the change in j which parallels the change in k, and the line intensities decrease in the order that the transition of j deviates from that of k. According to the interval rule[7] odd multiplets have integral interval proportions 1:2:3:4 . . . while in even multiplets the interval ratios are proportional to 3/2:5/2:7/2:9/2 . . . In other words, in systems of odd permanent multiplicity a term difference $\Delta\nu_{j,j+1}$ is proportional to $j+1$, and in even systems to $j+1/2$. The intensity rule and especially the interval rule are not infrequently violated but they are nevertheless important aids in the analysis and interpretation of spectra.

III. VERIFICATION OF THE DISPLACEMENT LAW

It is well known that the arc spectra of the alkali metals are characterized by doublets and those of the alkaline earths by singlets and triplets while the spark spectra of the latter show doublet structure.[8] For example, the Fraunhofer lines H and K due to ionized calcium are comparable with the Fraunhofer lines D_1 and D_2 of neutral sodium or the corresponding doublet in the arc spectrum of potassium. A partial analysis of the spark spectrum of potassium by Nissen[9] indicates that this spectrum resembles the arc spectrum of argon in accordance with the displacement law.

From this point we may proceed to present the evidence for the displacement law of arc and spark spectra by giving examples of regularities in spark spectra of scandium, titanium, vanadium, chromium, manganese and iron in the order named.

Tables 1 to 6 inclusive, give multiplet structures at the margin of which the combining spectral terms are indicated together with their separations in wave-numbers. The individual spectral lines are represented by their observed wave-lengths (in air), above which their relative intensities and temperature classes appear while the corres-

[8] Fowler, Series in Line Spectra, 1922; Paschen and Götze, Seriengesetze der Linienspektren, 1922.

[9] Nissen, Astroph. Jour., *57*, p. 185; 1923.

investigations for the purpose of analyzing complex spectra and especially for the separation of spark from arc lines. The letter *E* which often follows the temperature class indicates that the line is recognized as "enhanced." When an asterisk precedes the wave length it means that the line belongs to the class known as *raies ultimes*,[10] the most sensitive lines from the standpoint of practical spectrochemical analysis.

SPECTRUM OF IONIZED SCANDIUM (Sc^+)

In 1914 a combination group of the type *D P* composed of six lines (2540.87—2563.23 A) was recognized by Popow[11] in the spark spectrum of scandium. Catalán[12] in 1922 published seven multiplets belonging to this spectrum but the types of terms involved in three of them were incorrectly named. The correct identification of terms was pointed out to us by Professor H. N. Russell who also found another multiplet (3352.08—3372.14 A). The wave-lengths and intensities of the eight multiplets in Table 1 are taken from unpublished values determined at the Bureau of Standards. The temperature classes and "enhanced" symbols are taken from King.[13] There are no published Zeeman-effect data for this spectrum but the remaining rules for multiplet structures are so nicely obeyed in Table 1 that there can be no question about any of the relations. Even the interval rule applies with a relatively high degree of exactness except to the *P* term with separations 5.94 and 81.80. The *raies ultimes* occur in a *D F* combination and it is evident that the *D* term with separations 67.65 and 109.97 corresponds to the lowest energy state in the ionized atom of scandium. In addition to these triplet system multiplets which include most of the strong lines of the spark spectrum, there are a few apparently isolated lines (e.g., 4246.83, 100 III *E*; 5031.02, 40 *VE*; 5526.82, 75 *VE*) which must be regarded as singlets. The structure of the spark spectrum of scandium is thus seen to resemble that of the arc spectrum of calcium.

[10] de Gramont, Compt. Rend., *171*, p. 1106; 1920.
[11] Popow, Ann. d. Phys., *45*, p. 163; 1914.
[12] Catalán, Anales Soc. Españ. Fis. y Quim., *20*, p. 606; 1922.
[13] King, Astroph. Jour., *54*, p. 199; 1921.

TABLE 1.—*Multiplets in the Spectrum of Sc⁺*

	D_3^3	109.97	D_2^3	67.65	D_1^3
	60,II				
F_4^3	*3613.84				
	27663.56				
238.86					
	30,III		50,II		
F_3^3	3645.31		*3630.76		
	27424.70		27534.65		
158.72					
	3,III		25,III		40,II
F_2^3	3666.54		3651.80		*3642.79
	27265.96		27376.01		27443.68
	50,II		20,II		
D_3^3	3572.53		3558.55		
	27983.40		28093.37		
139.82					
	20,II		35,II		20,II
D_2^3	3590.48		3576.35		3567.70
	27843.53		27953.55		28021.25
103.52					
			20,II		30,II
D_1^3			3589.64		3580.94
			27850.01		27917.73
	20,III		10,III		3,IV
P_2^3	3372.14		3359.68		3352.08
	29646.24		29756.24		29823.95
81.80					
			15,III		10,III
P_1^3			3368.94		3361.26
			29674.44		29742.20
5.94					
					12,III
P_0^3					3361.94
					29736.23
	10		5		1
P_2^3	2552.38		2545.24		2540.87
	39167.41		39277.21		39344.74
230.39					
			9		6
P_1^3			2560.26		2555.84
			39046.84		39114.33
112.74					
					8
P_0^3					2563.23
					39001.59

	P_2^3	52.94	P_1^3	27.46	P_0^3
	25, *V E*				
D_3^3	6245.64				
	16006.73				
139.82					
	8		20		
D_2^3	6300.70		6279.74		
	15866.87		15919.84		
103.52	1		8		15
D_1^3	6342.08		6320.86		6309.90
	15763.34		15816.28		15843.74
	25, *V E*		15, *V E*		
P_2^3	5657.89		5640.99		
	17669.55		17722.48		
81.80					
	12, *V E*		9, *V E*		8, *V E*
P_1^3	5684.21		5667.16		5658.35
	17587.72		17640.65		17668.10
5.94					
			10, *V E*		
P_0^3			5669.05		
			17634.75		
	F_4^3	104.21	F_3^3	80.68	F_2^3
	40,III *E*		5, *V E*		
F_4^3	4374.46		4354.60		
	22853.57		22957.79		
239.86					
	2		30,III *E*		6,IV *E*
F_3^3	4420.66		4400.38		4384.80
	22614.72		22718.92		22799.65
158.72					
			3, *V E*		20,III *E*
F_2^3			4431.35		4415.55
			22560.17		22640.91
	60,III *E*		8,IV *E*		1
D_3^3	4314.09		4294.77		4279.95
	23173.39		23277.60		23358.20
139.82					
			50,III *E*		10,IV *E*
D_2^3			4320.73		4305.71
			23137.76		23218.43
103.52					
					40,III *E*
D_1^3					4325.00
					23114.93

SPECTRUM OF IONIZED TITANIUM (Ti^+).

A very thorough analysis of the spark spectrum of titanium has been made by Prof. H. N. Russell and the multiplets given in Table 2 were selected from his manuscript with permission to use them here in advance of his own publication. Prof. Russell has arranged more than 300 spark lines in doublet and quartet multiplets, only three examples from each system being reproduced here. The structures are quite analogous to those which exist in the arc spectrum of scandium.[14] Instead of the normal state of neutral scandium being represented by a doublet P term as Catalán supposes, Russell[15] points out that it is probably of type D. In ionized titanium the lowest energy level is represented by the F term with separations 93.94, 131.53, and 167.75, the combination of this four-fold term with a four-fold G term containing the *raies ultimes*.

TABLE 2.—*Multiplets in the Spectrum of* Ti^+

	F_3^2 269.07 F_4^2	
	(2−VE)	(3−VE)
D_2^2	2868.73	2891.05
	34848.43	34579.34
243.48		
	(2−VE)	
D_3^2	2888.92	
	34604.95	
	(8−VE)	(40−IVEr)
F_4^2	3721.64	3759.30
	26862.29	26593.20
283.36		
	(40−IVEr)	(1−)
F_3^2	3761.32	3799.77
	26578.92	26309.86
		(20−IIIEr)
G_5^2		3349.02
		29850.93
205.23		
	Arc blend	
	(50r−II)	(5−VE)
G_4^2	3341.87	3372.20
	29914.77	29645.70

[14] Catalán, Anales Soc. Españ. Fis. y Quim, *20*, p. 606; 1922, Ibid *21*, p. 464; 1923.
[15] Russell, Contr. Mt. Wilson Obs. (in press).

	F_2^4 93.94	F_3^4 131.53	F_4^4 167.75	F_5^4
		(5−IV)	(30−III*Er*)	(60−III*Er*)
D_4^4		3059.73	3072.10	3088.03
		32673.12	32541.60	32373.77
69.08				
	(2−)	(30−IV*Er*)	(45−III*Er*)	
D_3^4	3057.43	3066.20	3078.64	
	32697.73	32604.20	32472.48	
95.43				
	(20−IV*Er*)	(40−III*Er*)		
D_2^4	3066.36	3075.22		
	32602.50	32508.59		
70.13				
	(40−III*Er*)			
D_1^4	3072.97			
	32532.38			
			(15−III*Er*)	(60−III*Er*)
F_5^4			3217.04	3234.52
			31075.49	30907.60
187.31				
		(15−III*Er*)	(50−III*Er*)	(20−III*Er*)
F_4^4		3222.82	3236.57	3254.23
		31019.78	30888.03	30720.36
154.91				
	(15−III*Er*)	(40−III*Er*)	(25−III*Er*)	
F_3^4	3229.18	3239.03	3252.85	
	30958.70	30864.58	30733.39	
122.18				
	(40−III*Er*)	(20−III*Er*)		
F_2^4	3241.97	3251.89		
	30836.60	30742.55		
				(40*r*−II*Er*)
G_6^4				*3349.41
				29847.45
272.60				
			(40*r*−III*Er*)	(15−III*Er*)
G_5^4			*3361.22	3380.28
			29742.61	29574.86
233.63				
		(30−III*Er*)	(15−III*Er*)	(4−IV*E*)
G_4^4		*3372.80	3387.83	3407.20
		29640.43	29508.97	29341.26
190.08				
	(40−III*Er*)	(15−III*Er*)	(5−IV*E*)	
G_3^4	*3383.76	3394.57	3409.80	
	29544.46	29450.40	29318.89	

SPECTRUM OF IONIZED VANADIUM (V^+).

The arc spectrum of titanium has been shown by Kiess and Kiess[16] to be built up mainly of triplet and quintet system multiplets, and Prof. Russell[17] has been able to identify terms in the singlet system. According to the displacement law the spectrum of ionized vanadium should contain similar structures. A partial analysis has revealed multiplets of the two systems first mentioned, of which the examples in Table 3 are typical, and the available Zeeman data indicate that singlets are also present in this spectrum. The *raies ultimes* of the vanadium spark occur in an F^5G^5 combination. The F level is no doubt the lowest one in this system but it cannot at present be stated positively that this represents the lowest energy level of ionized vanadium. In neutral vanadium the lowest level is represented by an F term of the quartet system and the arc *raies ultimes* occur in a combination of this F with a G term.[18]

The intensities and temperature classifications for the quintet system multiplets in Table 3 are taken from a manuscript to which Dr. King has kindly given us access in advance of publication.

TABLE 3.—*Multiplets in the Spectrum of* V^+

	F_4^3	234.55 F_3^3	193.80 F_2^3
	20	5	
F_4^3	3727.348	3760.230	
	26821.13	26586.59	
66.24			
	3	15	3
F_3^3	3718.163	3750.873	3778.359
	26887.38	26652.82	26459.02
51.81			
		3	10
F_2^3		3743.63	3770.976
		26704.48	26510.83

[16] Kiess and Kiess, J. O. S. A. & R. S. I., *8*, p. 607; 1924.
[17] Russell, (in press).
[18] Meggers, Journ. Wash. Acad. Sci., *13*, p. 317; 1923.

	F_5^5 194.56	F_4^5 159.54	F_3^5 121.78	F_2^5 82.20	F_1^5
	40,III *Er*				
G_6^5	*3093.10				
	32320.62				
290.33					
	20,IV *E*	40,III *Er*			
G_5^5	3121.144	*3102.301			
	32030.29	32224.82			
246.55					
	.....	25, IV *E*	30, III *Er*		
G_4^5	3145.35	3126.221	*3110.710		
	31783.74	31978.27	32137.71		
200.82					
		5, V *E*	25, III *E*	30, III *Er*	
G_3^5		3145.979	3130.270	*3118.382	
		31777.43	31936.91	32058.65	
153.02					
			10 IV *E*	20, III *E*	40, III *Er*
G_2^5			3145.344	3133.336	*3125.286
			31783.86	31905.67	31987.84
	30, IV *Er*	15, IV *E*			
F_5^5	2924.024	2907.470			
	34189.47	34384.11			
201.94					
	10, IV *E*	25, IV *Er*	10, IV *E*		
F_4^5	2941.39	2924.654	2911.056		
	33987.59	34182.11	34341.77		
231.47					
		20, IV *E*	15, IV *E*	8, IV *E*	
F_3^5		2944.59	2930.813	2920.384	
		33950.67	34110.27	34232.09	
245.74					
			20, IV *E*	5, IV *E*	8, IV *E*
F_2^5			2952.079	2941.50	2934.410
			33864.56	33986.32	34068.47
184.04					
				10, V *E*	10, V *E*
F_1^5				2957.527	2950.34
				33802.19	33884.52

SPECTRUM OF IONIZED CHROMIUM (Cr^+).

In Table 4 are given three multiplets from the quartet system, two from the sextet system and one inter-system combination, of the chromium spark spectrum. These are representative of many others which have been recognized. The available Zeeman-effect data indicated the presence of doublets also, in which case the spectrum of ionized chromium will be parallel to that of neutral vanadium, which now has about 800 of its lines arranged in doublet, quartet and sextet

system multiplets.[19] The spark *raies ultimes* of chromium are in a D^6F^6 multiplet, the D^6 term being the lowest thus far found in the ionized atom.

TABLE 4.—*Multiplets in the Spectrum of* Cr^+

	D_1^4	103.04	D_2^4	166.72	D_3^4	226.08	D_4^4
			3		10		20
P_3^4			3324.06		3342.58		3368.04
			30075.10		29908.42		29682.40
141.76							
	3		10		10		
P_2^4	3328.34		3339.80		3358.50		
	30036.43		29933.31		29766.69		
71.89							
	5		6				
P_1^4	3336.33		3347.83				
	29964.43		29861.53				
					3		5
D_4^4					2857.40		2875.99
					34986.56		34760.49
158.77							
			3		5		3
D_3^4			2856.76		2870.43		2889.19
			34994.40		34827.79		34601.72
126.23							
	2		2		4		
D_2^4	2858.62		2867.09		2880.89		
	34971.64		34868.35		34701.38		
81.81							
	2		2				
D_1^4	2865.33		2873.83				
	34889.77		34786.60				
							20
F_5^4							3132.04
							31918.91
154.02							
					20		5
F_4^4					3124.97		3147.22
					31991.10		31764.89
119.52							
			15		5		1
F_3^4			3120.36		3136.69		3159.10
			32038.34		31871.49		31645.47
85.03							
	10		5		2		
F_2^4	3118.65		3128.68		3145.07		
	32055.91		31953.17		31786.60		

[19] Meggers, Loc. Cit. and unpublished results.

	D_1^6	70.80	D_2^6	115.22	D_3^6	156.03	D_4^6	192.66	D_5^6
					3		10		15
P_4^6					2740.10		2751.86		2766.54
					36484.24		36328.37		36135.52
140.95									
			8		10		10		
P_3^6			2742.02		2750.72		2762.59		
			36458.69		36343.41		36187.31		
92.18									
	8		8		8				
P_2^6	2743.64		2748.98		2757.71				
	36437.17		36366.41		36251.33				
			5		3		6		
P_3^4			2653.59		2661.74		2672.84		
			37673.58		37558.27		37402.33		
141.76									
	4				8				
P_2^4	2658.60		.....		2671.82				
	37602.61		.....		37416.61				
71.89									
	3		6						
P_1^4	2663.68		2668.72						
	37530.91		37460.06						
									30
F_6^6									*2835.64
									35255.09
287.00									
							15		4
F_5^6							*2843.24		2858.91
							35160.88		34968.09
237.46									
					10		10		2
F_4^6					*2849.84		2862.59		2878.44
					35079.35		34923.15		34730.90
186.80									
			10		4		3		
F_3^6			*2855.67		2865.11		2877.98		
			35007.76		34892.45		34736.46		
135.19									
	5		5		3				
F_2^6	2860.93		2866.75		2876.25				
	34943.41		34872.49		34757.34				
81.70									
	5		3						
F_1^6	2867.64		2873.48						
	34861.67		34790.84						

SPECTRUM OF IONIZED MANGANESE (Mn^+).

Catalán[20] in his investigation of the spectra from manganese discovered four groups in the spark spectrum of this element. These were given interpretation on the basis of Zeeman effect by Back[21] who found that two of them belong to the quintet system and the remainder to the septet system. The data are presented in Table V. The spark *raies ultimes* occur in the S^7P^7 combination. The relative magnitudes of the quintet and sextet terms have not been published.

TABLE 5.—*Multiplets in the Spectrum of* Mn^+

	P_3^5	114.07	P_2^5	72.50	P_1^5
	10, IV		9, V		8, V
S_2^5	2949.207		2939.315		2933.066
	33897.54		34011.62		34084.07
	9, V				
D_4^5	3441.999				
	29045.93				
269.28					
	7, V		8, V		
D_3^5	3474.050		3460.332		
	28776.65		28890.71		
187.34					
	4, V		7, V		6, V
D_2^5	3496.815		3482.918		3474.13
	28589.30		28703.37		28775.90
120.00					
			6, V		8, V
D_1^5			3497.540		3488.618
			28583.37		28655.89
58.63					
					8, V
D_0^5					3495.840
					28597.26

[20] Catalán, Phil. Trans. Roy. Soc. London, A *223*, p. 127; 1922.
[21] Back, ZS. für Physik. *15*, p. 206; 1923.

	P_4^7	263.58	P_3^7	176.91	P_2^7
	10		9		9
S_3^7	*2576.116		*2593.734		*2605.695
	33806.52		33542.94		33366.03
	10				
D_5^7	2452.53				
	40761.9				
10.6					
	2		5		
D_4^7	2453.17		2437.45		
	40751.3		41015.7		
9.0					
	1		3		3
D_3^7	2453.65		2437.92		2427.43
	40743.0		41006.1		41183.3
4.4					
			3		4
D_2^7			2438.22		2427.77
			41001.1		41177.5
3.4					
					4?
D_1^7					2427.97
					41174.1

SPECTRUM OF IONIZED IRON (Fe^+).

The spectral structures for neutral manganese belong to systems which attain even permanent multiplicities (quartets, sextets and octets) and in order that the displacement law may be extended to column VIII we must find even structures in the spark spectrum of iron. That this has been accomplished is shown by Table 6 which contains examples of quartet and sextet multiplets in the spectrum of ionized iron. The lines with asterisks in the D^6D^6 multiplet are sensitive in the quantitative spectrum of iron according to Pollok and Leonard,[22] but they are not the *raies ultimes* according to de Gramont. The latter are 2382.04 and 2395.63 A, but the combination of terms involved by them has not yet been determined. The D^6 term with separations 114.38, 194.98, 282.88, 384.80 is probably the lowest level in the sextet system and may be assumed for the present to represent the normal state of the ionized iron atom. In this connection it is recalled that the normal state of the neutral atom of iron[23] was shown to be represented by a term of type D^5.

[22] Pollok and Leonard, Roy. Dublin Soc., Sci. Proc., *11*, p. 221; 1907.
[23] Walters, J. O. S. A. & R. S. I., *8*, p. 245; 1924.

No evidence for either doublet or octet system multiplets among the spark lines of iron has yet been found and it is doubtful if the present state of the spectral data will permit a complete analysis. This problem is now in the hands of Prof. Russell and the staff of the Mt. Wilson Observatory.

TABLE 6.—*Multiplets in the Spectrum of Fe^+*

	D_4^4 436.51	D_3^4 288.50	D_2^4 166.23	D_1^4
	5	4	2	
P_3^4	2562.541	2591.549	2611.08	
	39011.94	38575.43	38286.91	
422.30				
		4	4	1
P_2^4		2563.484	2582.590	2593.528
		38997.73	38709.24	38543.03
236.34				
			3	3
P_1^4			2566.916	2577.92
			38945.60	38779.35

	D_5^6 201.06	D_4^6 198.95	D_3^6 154.26	D_2^6 96.11	D_1^6
	20	10			
D_5^6	*2599.405	*2585.885			
	38458.86	38659.93			
384.80					
	5	10	8		
D_4^6	2625.676	*2611.885	*2598.377		
	38074.08	38275.12	38474.09		
282.88					
		3	6	10	
D_3^6		2631.332	2617.624	*2607.098	
		37992.26	38191.19	38345.53	
194.98					
			4	3	8
D_2^6			2631.053	2620.419	2613.835
			37996.30	38150.47	38246.57
114.38					
				8	4
D_1^6				2628.300	2621.674
				38036.08	38132.20

The above evidence is sufficient proof that the displacement law is valid throughout the periodic system of the chemical elements. It shows furthermore that the various rules governing spectral structures apply to spark spectra as well as to arc spectra from which they were in large measure empirically derived. The Zeeman-effect observations, as far

as they go, are in excellent accord with the theory of Landé. In this connection we wish to thank Mr. Babcock of the Mt. Wilson Observatory for kindly lending us his unpublished data on Zeeman effects for vanadium, chromium and iron which have been of great value in discovering spectral terms and confirming the arrangement of multiplets in these complex spectra.

The combination rules for quantum numbers k and j are obeyed without exception in the examples quoted above. Qualitative if not exact agreement with the interval rule occurs with few exceptions. The intensity rule is obeyed in general except for certain combinations in which two terms are of multiplicity exceeding four. In the latter case the line corresponding to the transition $j \rightarrow j$ when $j = 2$ often appears to be abnormally weak. Attention was first called to this fact in two D^6D^6 multiplets of neutral vanadium,[24] and was observed also in a combination D^7D^7 of neutral iron. The same phenomenon is observed in spark spectra and is illustrated by the D^6P^4 multiplet in Cr^+, the F^5F^5 multiplet in V^+, and the D^6D^6 multiplet in Fe^+, which are given above.

The advances which have been made in the interpretation of spectra now enable us to draw some general conclusions as to the relation of the empirical *raies ultimes* to spectral terms. In the above example of spark spectrum multiplets, it is observed that the most sensitive spark lines occur without exception, among terms belonging to systems of the largest permanent multiplicity observed in the particular spectrum, and in all cases where the relative term magnitudes are known or temperature classification of the lines exists it is seen that these *raies ultimes* involve the lowest energy level, i.e., the normal state of the ionized atoms. The *raies ultimes* of the spark spectra of yttrium and zirconium have been found to be strictly analogous to those for scandium and titanium.

That the *raies ultimes* of arc spectra, on the other hand, exhibit less uniform relations to term multiplicities and magnitudes is seen in the following facts. The most sensitive lines of elements in column I, whose spectra consist of doublets, are the first members of the doublet principal series. Elements of column II whose spectra are composed of singlet and triplet systems have their *raies ultimes* in the singlet system, while elements in column III whose spectra consist of doublets or of doublets and quartets show *raies ultimes* only in the doublet systems.

[24] Meggers, Journ. Wash. Acad. Sci. *13*, p. 317; 1924.

The arc spectrum of titanium (column IV) which comprises singlets, triplets and quintets has its *raies ultimes* in the quintet system, and the same is true for zirconium. The *raies ultimes* for vanadium (column V) occur in an F^4G^4 combination; for chromium and molybdenum (column VI) they occur in S^7P^7 triplets; for manganese (column V) they are in an S^6P^6 triplet, and iron (column VIII) contains its most sensitive arc lines in a D^5F^5 multiplet. In almost every case where the relative terms are known these sensitive lines of arc spectra involve the lowest energy level, but an interesting exception to the rule that *raies ultimes* are related to the normal state of the atom occurs in column IV. The group of titanium lines 4981.73 to 5014.28 A (F^5G^5) were found by de Gramont to be very much more sensitive than the lines 5173.74, 5192.97, 5210.39 A (F^3F^3), and this has been confirmed by our experience in spectrochemical analysis. The intersystem combinations, however, show that the lowest triplet F term is 6500 wave-numbers lower in the energy diagram than the lowest quintet F term. In general, true *raies ultimes* never occur in combinations between terms of the same type nor in intersystem combinations although such transitions may involve the lowest energy level and smaller energy changes. Transitions of these types appear to be less probable than the lowest combinations in the particular system containing the *raies ultimes*.

The present state of knowledge as to the types of regularities existing in the arc and spark spectra of the elements with atomic numbers 19 to 26 which have been under discussion in this paper, is summarized in Table 7. To date no more than three systems of structures have been found in any spectrum and it remains to be seen if this is the maximum number which can be attained.

The authors have been interested in extending the search for spectral regularities and test of spectroscopic laws to the elements in the first half of the second long period. These elements are rubidium, strontium, yttrium, zirconium, columbium, molybdenum, (eka manganese), and ruthenium whose atomic numbers are 37 to 44 in the order named. Even structures have been found in the arc spectrum of yttrium while its spark spectrum exhibits singlets and triplet systems like the arc spectrum of strontium. The structures in the arc and spark spectra of zirconium parallel those of titanium which have been described above. Even systems have been found in the arc spectrum of columbium and regularities belonging to quintet and septet systems have already been

published for the arc spectrum of molybdenum.[25] Further details will appear in future papers, but it is of interest to note here that in so far as the investigations have been successful they indicate that exactly the

TABLE 7

SYSTEMS OF REGULARITIES FOUND IN ARC SPECTRA.

Column	I	II	III	IV	V	VI	VII	VIII
Element	K-19	Ca-20	Sc-21	Ti-22	V-23	Cr-24	Mn-25	Fe-26
Systems	Doublet	Singlet Triplet	Doublet Quartet	Singlet Triplet Quintet	Doublet Quartet Sextet	Triplet Quintet Septet	Quartet Sextet Octet	Triplet Quintet Septet

SYSTEMS OF REGULARITIES FOUND IN SPARK SPECTRA.

Column	I	II	III	IV	V	VI	VII	VIII
Element	K-19	Ca-20	Sc-21	Ti-22	V-23	Cr-24	Mn-25	Fe-26
Systems		Doublet	Singlet Triplet	Doublet Quartet	Singlet? Triplet Quintet	Doublet? Quartet Sextet	Quintet Septet	Quartet Sextet

same spectroscopic laws apply to the second long period of chemical elements as have been shown in this paper to be valid for the elements of the first long period.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
JUNE 28, 1924.

Relative Intensities of the Components of Multiple Lines.—The measurements, made by the photographic method, are upon: (a) two doublets each of the sharp and diffuse series of Na, K, and Rb, and one doublet of each subordinate series of Cs; (b) one triplet of the diffuse series of Mg, Ca, Zn, and Cd; (c) a triplet of the sextet system and another of the octet system of Mn. The striking thing is that the intensity ratios of the components are—so far as the accuracy of the measurements, which is moderately good, permits—ratios of small integers 2:1 in case (a), 5:3:1 in case (b), 4:3:2 and 5:4:3 in the two cases (c). These values are independent of the intensity of the arc-current. They are in accordance with certain expectations.—[H. B. Dorgelo, Utrecht; ZS. f. Phys. *22*, pp. 170-177; 1924.]

K. K. DARROW

[25] Kiess, Sci. Pap. Bur. Stds., *19*, p. 113; 1923, Catalán, Anales Españ. Fis. y Quim. *21*, p. 213; 1923.

THE REFLEX ORIGIN OF COLOR CONTRAST

By Frank Allen

SYNOPSIS

In this paper the principle of sensory reflex action is applied to the explanation of color contrast by the method of Ragona Scina. Abney's experiment in which he found the contrast color induced on a white surface by green to be orange instead of the complementary purple is also explained. Consideration is also given to binocular contrast.

The theories of contrast of Helmholtz, Edridge-Green, McDougall, Mrs. Ladd-Franklin, Hering and Sherrington are briefly discussed.

In two papers recently published[1], the writer showed by numerous experimental measurements that every ray of light falling upon the retina produces both direct and reflex effects on the three fundamental sensations, red, green, and violet. The former, or direct action of a color, stimulates and, at the same time, depresses or fatigues the three sensations in very unequal amounts, and is the effect of light or color usually perceived and studied. The latter, or reflex action, enhances the sensitiveness of the three sensations in the retinal area directly excited, in the adjoining regions of the same retina, and is also transferred to the other eye with the same enhancing effect.

The enhancement, while extending to all three sensations, predominantly affects those complementary to the sensations stimulated by the direct action of the color. For example, red light, by its direct action, chiefly affects the red sensation, and to a far less extent the green and violet; by its reflex action it enhances all three sensations, but predominantly the green and violet, which together are the complementary of red.

Since darkness adaptation of the unused eye produces effects that neutralize the enhancement of brightness caused by reflex action, these researches were conducted in a room lighted by ordinary daylight, so that the unused eye was always maintained in daylight adaptation.

This reflex principle, coupled with the trichromatic theory, was shown by the writer to afford a physiological explanation of the modification of lights and colors by contrast. If, for example, contiguous patches of yellow and green colors are viewed by one eye fixated on a point in the junction of the two areas, the yellow light reflexly enhances the sensations producing its complementary, blue, in the retinal area occupied by the green, which is thereby perceived as if it were mixed with blue.

[1] On Reflex Visual Sensations. J. O. S. A. and R. S. I. 7, p. 583; 1923.
On Reflex Visual Sensations and Color Contrast. J. O. S. A. and R. S. I. 7, p. 913; 1923.

Similarly, green enhances its complementary sensations, red and violet, in the area upon which the yellow light falls, causing that color to appear as if mixed with purple. Thus each color is perceived as if mixed to a greater or less extent with the complementary of the other, an effect which in general gives them the appearance of being moved away from each other in the spectrum. Two colors which are complementary will obviously be modified chiefly by having their saturation deepened or increased.

It should be noted, however, that the complementary effect of contrast is only a predominant action, for the visual reflex enhances all three sensations.

It is to be expected therefore from the reflex principle that slight departures from the complementary character of contrast will always occur. This is well recognised by color theorists, as Parsons[2], for example, shows in his statement that "under ordinary circumstances the induced color is not the precise complementary of the inducing, as was known to Goethe, and has been fully investigated by Hering."

In the former paper on contrast to which reference has been made, several of the most illustrative examples ofcontrast phenomena were discussed and explained by the new reflex principle. In this communication some additional contrast experiments of various observers are considered and the reflex theory also applied to explain them.

One of the most effective modes of obtaining contrast is that devised by Ragona Scina. For some time the writer found difficulty in reconciling this contrast effect with the explanation on the reflex principle. Rood[3] has described this important method in such detail that the writer ventures to quote from him.

"Two sheets of white cardboard are attached to a couple of boards fastened together at a right angle, as indicated in Fig. 1. Between the boards a plate of rather deeply coloured glass, G, is to be held at an angle of 45°. If the eye is placed at E, two masses of light will be sent to it. From the vertical cardboard white light will start, and, after being reflected on the glass plate, G, will reach the eye. This light will be white, or almost entirely white, since it is reflected from the upper surface of the coloured glass plate. The second mass of white light will proceed from the horizontal sheet of cardboard, H, and after traversing the plate, G, will become coloured by absorption. If the glass plate is red, this light when it reaches the eye will of course have the same colour; consequently the first result is that we have presented to the

[2] Colour Vision. p. 128; 1915.
[3] Colour or Modern Chromatics, 3rd Ed., p. 257.

eye a mixture of red with white light, which will give the observer the idea that he is looking at a horizontal, square field of a somewhat pale reddish tint. If now a small black square be attached to the vertical cardboard at B, of course no white light can come to the eye from this portion of the cardboard and the image of this spot will seem to the eye to be at *b* on the horizontal board under the eye. Under ordinary circumstances this image would appear black; in point of fact, however, in this case it appears deep red, owing to the red light transmitted by the plate of glass. Thus far the arrangement amounts to a device for presenting to the eye a mixture of red with white light, the white light being absent at a certain spot, which consequently appears of a deeper red. A similar black square is now to be placed on the horizontal board at C; it will of course prevent the light from the place it covers from

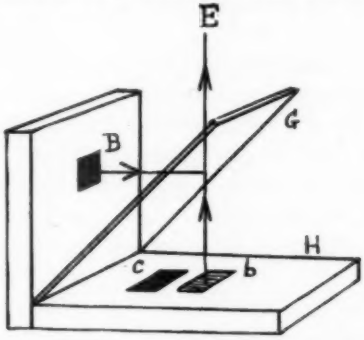

FIG. 1. *Contrast method of Ragona Scina.*

reaching either the red glass or the eye, and under ordinary circumstances would be perceived simply as a square black spot. Owing, however, to the fact that the upper surface of the glass plate is reflecting white light to the eye, it really appears as a grey spot. The final result is that we present to the eye at E a pale-red ground on which is a spot of pure grey, and near it one which is deep red. Owing to contrast, however, the appearance is different: instead of a grey spot, we see one strongly coloured green-blue. This effect is partly due to contrast with the pale-red of the ground, but still more to the presence of the deep-red spot. This latter we can remove by taking away the black square, B, which diminishes the effect considerably. But now comes the most curious part of this experiment; if we select a square of grey paper which has the same colour with the grey square seen in the apparatus, apart from the effects of contrast, and place it *over* the glass plate and near the other two images, it will not be affected in colour, or only to a

slight extent. In point of fact, we now have, *side by side*, on the same field, two grey squares quite identical in actual colour, but one appears by contrast blue-green, while the other is not affected, but is perceived by the eye as being simply a square of grey paper. *As soon, however, as* the observer recognizes the fact that these two squares really have the same grey colour, the illusion instantly vanishes, and both of them remain persistently grey. It is evident that in this case, as with coloured shadows, the judgment is at fault rather than the retinal nerves; for *as soon as* an opportunity offers, it corrects itself and takes a new departure. The illusion in this case, as well as with the coloured shadows, is produced quite independently of the knowledge of the observer, who may indeed be a trained physicist, minutely acquainted with the facts of the case, and with all the details employed in producing the deception, and still find himself quite unable to escape from its enthrallment."

In order to understand the reflex actions involved in this experiment we must consider the complete color pattern on the retina. This consists of a pale red ground over the retinal periphery where it excites but little reflex effect, since its physiological intensity rapidly diminishes as the distance from the centre is increased.[4] In the central retina are three fairly large areas, one, a deep red, and two grey of equal intensities which, according to Rood's description, are "side by side". The greatest part of the contrast effect on the grey, as Rood points out, is due to the deep red patch, which is naturally brought about by directing vision between the red and grey areas.

In accordance with the reflex visual process outlined above, the red light enhances the sensitiveness of the three primary sensations, red, green, and violet, in the surrounding areas of the retina, but predominantly the sensations complementary to red. The white light from the grey patch falling upon the unequally excitable sensations, stimulates the green and violet more than the red, which results in the production of the bluish-green color observed.

The critical part of the experiment is contained in the words of Rood which the present writer has italicized in the quotation, particularly the expression: "*As soon as* the observer recognises", etc. Expressed in other words, this part of the description means that when vision is fixated on a point between the two *grey* squares, the image of the large red area then falls on the periphery of the retina, where its intensity and consequently its reflex effect are greatly reduced; and, as the words of

[4] Parsons: Colour Vision, Fig. 24, p. 69; 1915.

Rood imply, a *time* interval is allowed for the two grey areas to readjust their retinal actions, and for the reflex effect of the deep red to subside. As both greys are originally made of equal and low intensities, their reflex effects on each other are negligible. When the color contrast is reduced to a minimum, the experiment is resolved mainly into one on luminosity contrast.

In attributing this effect to illusion or deception of the judgment, Rood remarks again that it corrects itself "as soon as an opportunity offers". This expression also implies an interval of time, which in some contrast experiments is quite necessary.

It is probable, however, that careful observation will show both grey patches to be slightly tinged with the contrast green-blue color by reflex action of the surrounding pale red ground.

The ascription of Scina's contrast effects to deception of judgment is therefore an erroneous interpretation. The reflex principle not only nullifies the psychological theory of Helmholtz but also supplies a positive physiological action quite adequate to explain the phenomena.

The last sentence of Rood's description in which he remarks how even a trained observer "minutely acquainted with all the details employed in producing the deception", is quite unable to prevent himself from being deceived, is a strong tribute to the clarity and precision of the judgment in rendering a truthful verdict on the various actions and reactions involved in the experiment.

Abney[5] has described some observations on simultaneous contrast which, on first consideration, also appear contradictory to the action of the reflex principle.

In his work he used a white surface upon part of which fell a beam of light of any desired spectral color, and upon the contiguous area a bright white light from an electric arc, or from an Argand burner.

By this experimental arrangement he desired to determine the contrast color induced in the white area by the color on the adjoining surface. He found that the contrast color in all cases could be matched by a single spectral color when diluted with white light. He noted, however, that the induced color was not always the complementary of the active light. It was found, for example, that when green is the active color, the induced color upon the white surface is orange instead of purple, which is the complementary of green.

The contradiction, however, is only apparent, as further considera-

[5] Researches in Colour Vision, p. 121.
Proc. Roy. Soc. *56*, p. 221; 1894.

tion shows. The reflex effect of green light when it falls upon one retinal area enhances the sensibility of the complementary sensations in the adjoining areas. A purple color is therefore induced in effect upon the part of the retina receiving the image of the bright white light. Now purple is formed by excitation of the red and violet sensations, of which red is much the more prominent or effective. It is also well recognized that colors mixed with white light tend towards yellow. Abney himself says:[6] "In the red the colour becomes pinker as more of the white light is added, the scarlet becomes orange, the orange yellow, and the yellow green. The yellow-green does not suffer a change but as the green is approached it becomes yellower in hue. . . .as the violet is approached a very small quantity of white will make it appear nearly salmon-coloured. If the white light added be that of a paraffin lamp, the red became more orange, the scarlet, as before, orange. . . . "

By referring to the reflex color curves[7] of the present writer, it will be seen that when white light is used as the stimulus, the yellow-green part of the spectrum is conspicuously enhanced in brightness, an effect which is doubtless explanatory of the latter observations of Abney. The dilution of a color with white light can only mean that the three primary color sensations are directly stimulated in certain, probably equal, proportions by the white light, and simultaneously in other proportions by the color. The net result of all the stimulations is finally interpreted by the judgment as a modification of the original color. Abney's observations show a few of such changes in the hues of spectral colors.

If in Abney's contrast experiment purple light had been allowed to fall upon the bright white surface, the change to orange would have been immediately recognized as conforming to established principles. But white light formed by a mixture of all waves may become colored in two ways: first, by adding light of the desired color, second, by selectively enhancing the sensibility of the proper sensation or sensations by reflex action thereby compelling the waves of the color already in the white light to excite these color sensations to a much greater degree than the remainder. The purple color may be obtained by adding a suitable mixture of red and violet light, or by increasing the sensibility of the corresponding sensations. In Abney's experiment the latter is the mode employed. The sensation of purple is formed by the enhanced excitability of the red and violet sensations, due to the reflex action of green,

[6] Researches in Colour Vision. p. 255.

[7] "On Reflex Visual Sensations"—loc. cit. p. 598.

and it is simultaneously changed to orange by the characteristic modifying power of white light due also to reflex action.

There is therefore no conflict between Abney's contrast experiments, when completely analysed, and the explanation afforded by the application of the principle of the visual sensory reflex. We may indeed go further and say that in Abney's apparently contradictory experiment we have a most unexpected confirmation of the reflex principle in conjunction with the trichromatic theory.

In the paper by the writer "On Reflex Visual Sensations"[8] it was shown that the reflex effect of color stimulation of one retina was transferred to the other so as to produce enhancement of the sensibility of all three primary sensations, but predominantly of the complementary of the original color stimulus. It was then stated that this effect accounted for binocular contrast.

The usual experiment on binocular contrast found in works on color vision, is that of Hering, which is thus described by Luckiesh[9]: "Hering devised a most striking demonstration of binocular contrast. Red and blue glasses were placed in front of the two eyes respectively. The glasses sloped away from the eyes from the nasal to the temporal side. This permitted a control of saturation by introducing a white image from the sides by reflection. A black stripe on a white ground is doubled by increasing or decreasing the ocular divergence. The observed ground appears spotted, alternately blue and red, and sometimes a purplish white, which is due to retinal rivalry. The stripe seen through the red glass appears green and through the blue glass appears yellow."

When this experiment is analysed, however, it appears to have nothing to do with binocular contrast, but consists of two different experiments on uniocular contrast proceeding simultaneously.

Let us consider the retinal pattern formed by the eye with the red glass in front of it. The white light from the ground surrounding the black stripe passes through the red glass and produces upon the retina a red image with a black area in the central part. The red light by reflex action enhances the sensitiveness of the three sensations, red green, and violet, but predominantly the two latter, in the dark area. The white light from the side source, reflected by the surface of the red glass upon the retina, renders the red ground less saturated, and stimu-

[8] Loc. cit. p. 615.

[9] Colour and its Applications. p. 177.
See also: Burch, Physiological Optics, p. 86.

lates the green and violet sensations more than the red in the dark area, which therefore appears green or bluish-green in color.

Similarly in the other eye, the blue ground color predominantly enhances the excitability of the sensations producing the complementary yellow in the dark area, so that the white light from the side source causes that color to be seen.

Nothing in these effects therefore appears to differ from ordinary contrast, so that binocular contrast need not be invoked to explain the observations. Indeed each of the two experiments appears to be identical with the color contrast part of Ragona Scina's experiment which has been described above.

Probably each eye does affect the other to some extent; but the more powerful uniocular actions conceal the binocular from observation.

Myers, in his work on Psychology[10], correctly refers Hering's experiment to uniocular contrast, and in addition has described an undoubted binocular contrast effect."By fixating a nearer point, the student produces double images of a white stripe on a black background. He places a red glass before the one eye and an equally bright grey glass before the other. He observes if the image seen through the grey glass is tinged with green (the complementary colour to red). He then removes the red glass and observes that the image yielded by the eye which has been covered with the grey glass, becomes a well-marked red."

These effects may be explained as follows. The red light in one eye reflexly enhances all three sensations in the other, but more especially its complementary. The white light coming through the grey glass first stimulates the green sensation in excess of the others and proportionately fatigues it, but acts upon the red sensation to a much less degree. When the red glass is removed the selective enhancement of the sensations no longer operates, and the white light then excites the red sensation more than the others, since it has been less fatigued.

In uniocular contrast a similar phenomenon is observed to which a similar explanation applies, except that two areas of a single retina are involved instead of the two eyes. To quote Myers[11] again: "But these effects (complementary) of simultaneous contrast disappear on prolonged fixation and are replaced by others of a directly opposite character. The surface, which at the beginning of fixation had evoked a con-

[10] Text-Book on Experimental Psychology, Part II.
Experiments 133 and 131, pp. 87 and 86; 1923.
See also: Schafer, Text Book of Physiology, *2*, p. 1098; 1900.
[11] Loc. cit. Part I. p. 76.

trast colour or brightness, now induces its own colour or brightness. This is termed simultaneous induction."

In passing we may refer to two other binocular phenomena. In the words of Myers[12]: "We have yet to explain why a steady image is able, while a flickering image is unable, to affect the image of the corresponding area of the other eye." And: "The brightness of the combined image of two steady flickerless lights, respectively thrown on corresponding retinal areas, is obviously not equal to the sum of the two brightnesses. Its value is usually slightly above the arithmetical mean of the brightness of the uniocular components, provided that these do not differ too widely from one another. When the components are equally bright, the binocular increase has been variously estimated to be from one-tenth to one-thirtieth."

The reflex curves of the writer[13] show that the reflex effect of light transferred from one eye to the other, causes enhancement of the brightness, except when the light is dim, in which case the brightness is diminished. But time is an essential factor in producing results to a measurable degree. The separate flashes of a flickering light in one eye have too little time in which to enhance sufficiently the brightness of the light in the other. Another effect also must not be overlooked. Darkness adaptation of one eye diminishes the brightness of light in the other. A flickering light produces intervals of darkness alternating with light, and the two effects nullify each other. Therefore both phenomena noted by Myers are in conformity with the reflex principle.

It has long been known that white tissue paper spread over the two contiguous color areas accentuates the contrast effect. This admits of easy explanation by the reflex theory. Each of the two contrasting colors enhances its complementary sensations in the area of the retina occupied by the other. Both colors stimulate their own sensations, and to a limited extent the enhanced sensations as well. The tissue paper, however, reflects upon the active retinal areas a small amount of white light which contains all the colors of the spectrum. An additional stimulus for each enhanced sensation is thereby provided, and the reciprocal modification of the colors is rendered much more effective and complete. In general, the same function is performed by any mode of reflecting white light into the eye so as to cover the areas of the contrasting colors.

[12] Loc. cit. p. 270.

[13] J. O. S. A. and R. S. I. 7, p. 583; 1923.

Contrast is a phenomenon of such fundamental importance that every theory of Color Vision must offer some explanation of it. And it is precisely this phenomenon which taxes the resources of every theory to the utmost degree.

In elaborating the trichromatic theory of Young, Helmholtz found it necessary to abandon the physiological actions entirely in regard to contrast, and therefore introduced the psychological theory of the systematic deception of the judgment. Many writers have shown the inadequacy of this explanation for uniocular contrast, and Myers[14], referring to binocular contrast, gives the conclusive objection that "one can hardly suppose that unconscious inferences arising from previous knowledge can be carried so far as to lead simultaneously to two different errors."

Edridge-Green[15] considers contrast at considerable length, and says: "My conclusion, therefore, is that the contrast colour developed in simultaneous contrast is due to the perception of an actual objective relative difference—in fact, the greatest difference which is perceptible in the circumstances, white being not a fixed objective quality, but a sensation produced by admixture of light of certain wave-lengths."

The writer is unable to grasp the meaning of this statement with sufficient clearness to apply it to any experiment on contrast. It appears, however, to regard contrast phenomena as purely psychological in their origin.

The color theory of McDougall "attributes simultaneous contrast to the inhibitory action of a given cortical visual process upon the visual process in the neighboring cortical regions."[16] If, for example, a grey surface with a red area upon it be fixated, the "highly excited activity of this red area depresses the activity of the red apparatus in the neighboring grey area of the cortex, whereby the blue and green in the latter area predominate over the red apparatus. . . .It is owing to this supposed inhibition of the red that the blue-green colour is produced."

If, however, the red is inhibited its brightness will be destroyed or diminished, while the blue-green will retain the same intensity as at first. But the experiments of the writer show definitely that, when bright, all colors are reflexly enhanced in brightness, and therefore no inhibitory process can be operative under these conditions. Many

[14] Loc. cit. p. 93.
[15] Physiology of Vision, p. 244.
[16] Myers: loc. cit. Part I, p. 94.

contrast experiments also are in harmony with this, and show a distinct brightening of the colors contrasted. But with contrast-darkening effects, which also are known, it is quite apparent that inhibition does occur. In these cases the sensory reflex arc would be suitable, and probably necessary, for that purpose. The theory of McDougall in this respect may therefore be partially correct; but the inhibition of colors under certain conditions is not at variance with the reflex principle, but rather confirms it.

Mrs. Ladd-Franklin offers a theory[17] of contrast which is highly mechanical and appears to involve quite impossible features. According to it the first color sensations were yellow and blue, which originated by differentiation of some of the primitive grey-molecules into color-molecules. In process of time the yellow molecules became further differentiated so as to be sensitive to action by waves of red and green.

In order to explain simultaneous contrast it is supposed, for example, that a red light will deprive large numbers of the color molecules of their red constituents, thereby leaving them partly mutilated and very unstable. The partially disintegrated molecules, however, still retain their green and blue constituents. These are swiftly conveyed in large numbers into the surrounding retinal areas where "their complete destruction causes the phenomenon of simultaneous contrast."

Parsons regards this explanation of contrast as unsatisfactory, largely for the reason that the retinal circulation conveying the mutilated molecules would have to be "almost instantaneous" over large areas to accomplish the purpose, and no such circulation is known to exist.

Since two contrasting areas of color modify each other, there must of course be two circulations in opposite directions. In general there must be as many circulations, or as many directions of the circulation, as there are contrasting colors in the field.

It is obvious that binocular contrast cannot be explained on this theory. No transfer of material particles from one eye to the other is possible.

The theory is unsatisfactory for another reason, since the assumed mechanism upon which the whole theory depends, is by its nature removed beyond the limits of experimental inquiry.

The theory of Hering may be summarised sufficiently for the present purpose by quoting from the description given by Myers.[18] "Hering assumes that there are two elementary systems, one of which gives rise

[17] Parsons: Colour Vision, p. 273; 1915.
[18] Loc. cit. p. 88

to red and green, the other to yellow and blue sensations, and that there is a third apparatus, excitation of which gives rise to the colourless series of sensations. According to this theory, the physiological actions of a colour stimulus and of its complementary colour stimulus are antagonistic. Red, for example, causes a katabolic (or dissimilation) change in the red-green apparatus, yellow a like change in the yellow-blue apparatus; green causes an anabolic (or assimilation) change in the former apparatus, blue a like change in the latter. The sensation of orange results from katabolism in the red-green and the yellow-blue apparatus, that of purple from katabolism in the former combined with anabolism in the latter apparatus.

"Each apparatus always tends to recover equilibrium, upon removal of the stimulus. After the red-green apparatus has been made to undergo dissimilation owing to the 'allonomous' action of a red stimulus, it proceeds to return to equilibrium by an 'autonomous' process of assimilation thereby developing the complementary after-sensation of green. Thus one colour sensation automatically evokes the opposite or complementary after-sensation.

"Hering explains the effects of simultaneous contrast by a similar principle. He supposes that the process of assimilation, set up by a stimulus in one part of the retina, brings about a process of dissimilation of the same apparatus in neighboring parts of the retina."

But what is the process or physiological mechanism by which an effect in one part of the retina brings about its opposite in another? Obviously, retinal circulation, diffusion, or a process of conduction, like heat conduction for example, cannot be operative, as they would have to be almost instantaneous in their action. Further it is not the same, but an opposite effect that the stimulated area of the retina induces in the surrounding regions.

Since the phenomena of binocular and of uniocular contrast are similar, the same explanation must apply to both. Hering's theory that a direct color process in one area of the retina automatically gives rise to an opponent complementary effect in the surrounding regions, must, therefore, if correct, include the same effect in the other eye as well. Hering assumed that dissimilation brings about assimilation of the photochemical substances, but did not show how it was done. As his theory stands, it fails to account for binocular contrast. But the principle of visual sensory reflex action renders it clear how areas in one as well as in both retinae, reciprocally affect each other. The reflex nervous impulses, with enhancing power upon the sensations, travel

back from the visual centres in the same time to all parts of each retina. Whether their effect on the visual receptor organs causes assimilation of some substance remains to be proved. Concerning this part of Hering's theory, the writer has no experimental evidence to offer. It may be suggested, however, that the reflex impulses acting on the receptor organs may produce a condition of selective instability in the photochemical substances so that certain waves may thereby be more effective than others in producing visual stimulation.

Sherrington[19] concluded from his extensive experiments on the binocular fusion of visual sensations and related phenomena that "only after the sensations initiated from right and left 'corresponding points' have been elaborated, and have reached a dignity and definiteness well amenable to introspection, does interference between the reactions of the two (left and right) eye-systems occur. The binocular sensation attained seems combined from right and left uniocular sensations elaborated independently." The further conclusion follows that binocular contrast and Fechner's paradox are due to a central mechanism where the separately elaborated retinal sensations are fused with consequent modification of their hue or brightness. With these conclusions the experiments of McDougall appear to be in accord.

The view advanced by the present writer is that a stimulus acting on one retina modifies the corresponding area of the other by enhancing or depressing the sensitivity of the visual receptors. This, it was suggested, is accomplished by a sensory reflex operating through a central mechanism.

Since it is found that uniocular contrast is similar to binocular, and that it is due to the same process, it follows that Fechner's paradox should also occur when two adjacent areas of a single retina are employed.

It is interesting and suggestive to note that Sherrington[20] also states that "The 'immediate spinal induction' exemplified by reflexes has a counterpart in visual irradiation. Visual contrast, if translated into terms of reflex contraction, bears close resemblance to 'successive spinal induction'. The features of fatigue repeat themselves in both sets of phenomena."

The increased sensitiveness of the sensations by reflex influence is apparent almost immediately after the direct stimulation begins. But

[19] Integrative Action of the Nervous System, p. 381.

[20] Ibid. p. 387. See also p. 208.

since fatigue or depression of sensitiveness also accompanies the direct action of color, a longer interval of time is required for the two actions to reach some condition of equilibrium. During this period changes in hue or brightness of a color will be observed, as the three sensations approach equilibrium in unequal times. In this way we may explain the changes in color which occur with time of fixation. When the direct action of light ceases, the reflex discharge may continue, and so produce the complicated series of negative after-images. This subject is too involved for present consideration. But it may be suggested generally that positive after-images are due to impulses which reach consciousness through stimulation of the afferent nerves; negative after-images are due to nerve discharges in the efferent portion of the reflex arc.

An effective conclusion to this paper may be found in the following remarks of Myers.[21] "The close resemblance of binocular to uniocular contrast compels us to suppose either that colour sensations are of more central origin than is commonly believed, or that a direct nervous connection exists between the two retinae whereby stimulation of one eye leads to retinal changes in the opposite eye. Such nervous connection has been demonstrated. Further, we know that movement of the cones, produced in one eye, leads to cone movement in the opposite eye. But this reaction is too slow to explain the immediacy of binocular contrast. It has been suggested that the electrical variation in the two eyes, which is known to occur after uniocular stimulation, may be the physiological basis of binocular contrast."

Further (p. 100), "Nothing is more certain than that, in addition to the more peripheral processes, central processes are also involved, in elaborating visual sensations. But at present we are powerless to separate the one from the other; we can only speak of changes in one vast unravelled complex,—the cerebro-retinal apparatus."

The nature of a visual sensory reflex arc involves central processes in Color Vision, one effect of which is the enhancement of the primary sensations in the retina. In this and other papers the writer has endeavoured to show that it is now possible to separate or distinguish the direct from the reflex actions of color, and so, it is hoped, to proceed one step farther in the unravelling process to which Myers alludes.

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[21] Loc. cit. p. 268

VISUAL SENSORY REFLEXES AND COLOR BLINDNESS

By A. Hollenberg

SYNOPSIS

Section I contains introductory remarks, and the consideration of the normal persistency curve of the author in order to determine the character of his type of color blindness.

Section II contains detailed descriptions of the reflex effects obtained in the right eye by fatiguing the left with colors of various wave lengths and with white light. The effect of darkness adaptation of the left eye upon color vision in the right eye is also studied.

Section III describes the direct effects of fatigue upon the right eye when colors and white light are used. Darkness adaptation of the right, or observing eye, is also considered.

In Section IV, various theoretical considerations are discussed with special reference to the bearing of the curves upon color theory. It is shown that the absence of reflex effects in the fatigue curves parallels the absence of negative after images in the author's eye.

The curves strongly confirm the trichromatic theory of Color Vision, and show that in explaining color blindness the assumption of a separate white sensation is unnecessary. The cause of color blindness seems also to be largely connected with the efferent nerve fibres, the actions of which are shown to be greatly interfered with, or even suppressed, in defective Color Vision.

I. The Normal Curve

This investigation was undertaken for the purpose of verifying the principle of the reflex enhancement of the visual color sensations recently discovered by Allen.[1] The writer was aware of some abnormality in his color vision, but did not know how much of the spectrum was involved. As the investigation proceeded, the full extent of the color deficiency became evident, and advantage was taken of the abnormal condition to study in detail the reflex and fatigue effects of various spectral colors.

The apparatus used was the same as that employed by Allen, which was fully described in his paper to which reference has just been made. By the method of measuring the duration of flashes of color at the critical frequency of flicker, persistency curves for the spectrum were obtained, first, when the right eye was in ordinary daylight adaptation, and, second, when it was under the direct or reflex influence of colors. Comparison of the last two types of curves with the normal enabled conclusions to be drawn regarding the action of different colors upon the visual sensations.

The first measurements were made to secure the normal or reference curve with which all others are compared. For this purpose the experiments were conducted in a room lighted by windows so that both

[1] On Reflex Visual Sensations. J. O. S. A. and R. S. I. 7, p. 583; 1923.

eyes were maintained in daylight adaptation. This was necessary since Allen found that darkness adaptation of one eye affected the other in such a manner as to counteract the reflex enhancement of the sensations.

The data for the normal curve are found in Table I together with similar measurements for all the reflex curves described in the next section.

TABLE I. *Reflex Curves*

λ	Normal	White Light	Darkness	Darkness and Pressure	.687μ
	sec.	sec.	sec.	sec.	sec.
.74μ	0.0386	0.0423	0.0334	0.0415	0.0421
.72	.0316	.0329	.0293	.0349	.0322
.70	.0266	.0273	.0254	.0280	.0273
.68	.0228	.0229	.0214	.0230	.0217
.66	.0182	.0185	.0178	.0185	.0189
.64	.0161	.0161	.0160	.0162	.0164
.62	.0146	.0150	.0144	.0152	.0145
.59	.0132	.0133	.0130	.0136	.0136
.57	.0130	.0131	.0125	.0133	.0131
.55	.0133	.0135	.0130	.0132	.0132
.53	.0137	.0138	.0135	.0136	.0142
.50	.0163	.0160	.0156	.0158	.0167
.48	.0194	.0189	.0189	.0186	.0187
.46	.0234	.0221	.0225	.0211	.0231
.44	.0295	.0287	.0272	.0276	.0304
.42	.0401	.0358	.0367	.0383	.0401
λ	.660μ	.589μ	.540μ	.450μ	.410μ
	sec.	sec.	sec.	sec.	sec.
.74μ	0.0352	0.0370	0.0383	0.0380	0.0401
.72	.0313	.0300	.0301	.0336	.0345
.70	.0269	.0256	.0258	.0264	.0283
.68	.0238	.0220	.0217	.0234	.0236
.66	.0179	.0185	.0185	.0180	.0203
.64	.0165	.0170	.0166	.0162	.0165
.62	.0147	.0150	.0147	.0149	.0147
.59	.0140	.0135	.0134	.0133	.0136
.57	.0134	.0135	.0133	.0134	.0130
.55	.0137	.0135	.0131	.0136	.0133
.53	.0146	.0143	.0139	.0142	.0135
.50	.0161	.0165	.0168	.0159	.0163
.48	.0194	.0187	.0192	.0189	.0192
.46	.0212	.0214	.0222	.0237	.0233
.44	.0270	.0263	.0265	.0281	.0276
.42	.0355	.0346	.0358	.0401	.0373

In order to discover the extent of the color deficiency, or blindness, as it is usually termed, the normal of the writer must be compared with one for the eye of a person with normal vision. A similar curve was made on the same spectrum and under precisely the same conditions by W. A. Anderson[2], whose color vision is normal trichromatic, except for a short interval of anomalous vision between the wave lengths .61μ and .68μ. The data for this curve are in Table 2.

TABLE 2. *Normal Persistency Curve.* (*W. A. Anderson*)

λ	*D*	λ	*D*	λ	*D*
	sec.		sec.		sec.
.74μ	0.0301	.64μ	0.0136	.50μ	0.0150
.72	.0249	.62	.0125	.48	.0187
.70	.0199	.59	.0111	.46	.0233
.68	.0158	.55	.0118	.44	.0300
.66	.0142	.53	.0126	.42	.0404

As his color vision is anomalous but not defective, Anderson's curve may be compared with the writer's and thus reveal the extent of the color blindness. The two curves are drawn to the same scale in Fig. 1. The continuous line is Anderson's normal, which in this paper is used only in this figure, and the dotted line is that of the writer. From this figure it is seen that the color vision of the writer is defective from the beginning of the red to the wave length .490μ. The violet portions of the curves coincide, which shows that this sensation is not defective in any way. The writer therefore is shown to be defective in both the red and green sensations. The neutral point is at the wave length .515μ, which is near the point where the two normal curves diverge. It is marked in the figure with an arrow.

In a detailed investigation of color blindness by this method, Allen[3] was able to classify twenty-six subjects into seven distinct types or classes: those defective in one sensation only, red, green, or violet; those defective in two sensations, red-green, red-violet, or green-violet; those defective in the three sensations, or the totally color blind. Six of the seven types were found and studied, but only with reference to their normal persistency curves. The missing type was violet blindness.

[2] On Reflex Visual Sensations and Anomalous Trichromatism. J. O. S. A. and R. S. I. 8, p. 731; 1924.

[3] Persistence of Vision in Color Blind Subjects. Phys. Rev. *15*, p. 193; 1902. Also: Persistence of Vision and the Primary Color Sensations. Am. Jour. Physiol. Op. *1*, p. 94; 1920

II. REFLEX CURVES

The first curves to be obtained were the reflex, in which the fatiguing color stimulus was applied to the left eye, and measurements of the critical frequency of flicker were made upon the right eye which remained in daylight adaptation. The curves obtained in this way are compared in the figures with the normal curve of the writer. The differences between the two curves must therefore be due to the effects of color transferred from one eye to the other. Allen[4] found that his reflex curves in all cases were below the normal, showing three depressions in the parts of the curves corresponding to the red, green, and

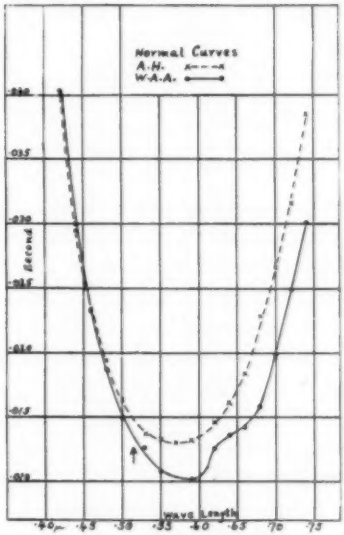

FIG. 1. *Normal curves.*

violet colors, which proved that these sensations were always reflexly enhanced in sensitiveness. These effects have been completely confirmed by M. S. Hollenberg,[5] who also worked in Allen's laboratory.

In no case did either of these observers find that the direct action of light was transferred from one eye to the other in excess of the reflex. Had it been transferred, it would have shown itself, it is presumed, by elevations of the curve above the normal, such as occur in the fatigue and reflex curves in this paper.

[4] On Reflex Visual Sensations. loc. cit.

[5] On the Verification of the Principle of Reflex Visual Sensations. J. O. S. A. and R. S. I. 8, p. 713; 1924.

In addition to these effects, Allen found six colors,. 660μ, .572μ, .520μ, .505μ, .480μ, and .425μ, which produced neither fatigue nor enhancement, so that the curves coincided with the normal. These were called equilibrium colors.

In the present investigation the red color .687μ was first used as the fatiguing stimulus on the writer's left eye. The curve obtained by the right eye is practically coincident with the normal in the part corresponding to violet, but small elevations occur in the portions of the curve corresponding to red and green. The departures from the normal are so slight that this color may almost be called an equilibrium color

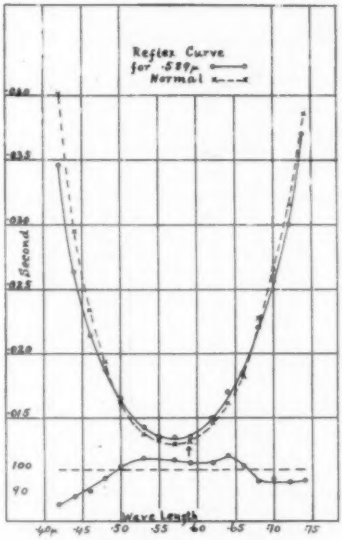

FIG. 2. *Reflex curve for .589μ.*

for the author. This is quite different from the normal eye, in which the first equilibrium color is .660μ, which lies at the end of the green sensation curves of Abney and of König. It may therefore be the case that in color blindness the green sensation curve extends more completely over the red sensation than in normal vision.

When the colors .660μ, .589μ, .540μ, and .450μ, were successively employed as fatiguing stimuli, curves similar to that in Fig. 2, for .589μ, were obtained. These are all of the same general type, showing depressions in the red and violet regions and an elevation in the green. The curve for the color .450μ, however, approximates the equilibrium

condition. It may be noted also that this color is not far from the point where the normal curves in Fig. 1 diverge, which is considered to mark the boundary between normal vision, and the defective color vision of the writer.

The curve obtained with the violet color .410μ has a depression in the violet and an elevation in the red, with scarcely any effect upon the green.

Almost exactly the same as this is the reflex curve obtained when white light was used as the fatiguing stimulus. This is shown in Fig. 3.

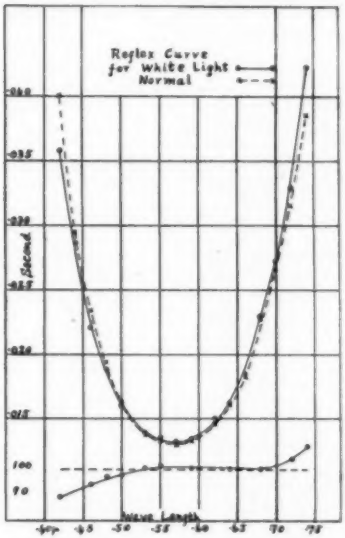

FIG. 3. *Reflex curve for white light.*

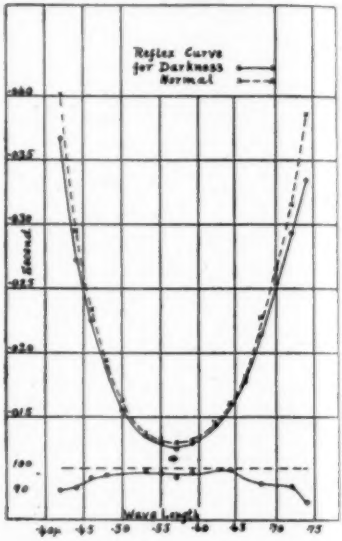

FIG. 4. *Reflex curve for darkness.*

In normal vision, darkness adaptation of the left eye caused the elevation of the whole curve above the normal, showing in consequence that the spectrum became physiologically less bright to the right eye. But in the writer's case, as is shown in Fig. 4, darkness adaptation caused a depression of the whole curve below the normal, indicating enhanced perception of all colors. But when pressure upon the left eye was added to its darkness adaptation, the green and red portions of the curve became elevated.

In Fig. 5 the reduced reflex curves obtained under all the above conditions are gathered together, and their uniformities and characteristics may be readily compared.

It was previously pointed out that the writer's vision was normal as regards the violet sensation. Allen found that in the normal eye reflex action enhanced the three fundamental sensations which depressed the curve in the parts corresponding to them. Since in the eye of the writer the violet sensation is normal, the part of the curve corresponding to it ought to be normal in its behavior and always show a depression. This is the case with all the curves except that for the red color .687μ, which is practically coincident with the normal. The violet sensation therefore conforms nearly perfectly with the theory. In four of the six reflex color curves the red portion is depressed and in two cases elevated,

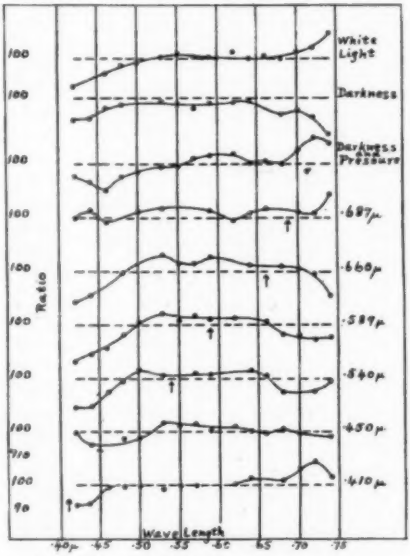

FIG. 5. *Reduced reflex curves.*

but the green is uniformly elevated. In other words, the green sensation always behaves abnormally, while the red is normal in its behavior with four colors in the middle of the spectrum, and abnormal with two which are the extreme red and extreme violet. With white light the violet sensation acts normally, and the red abnormally. Darkness adaptation is abnormal in its effect upon all the sensations. All the curves, however, show the usual threefold division corresponding to the three primary sensations, red, green, and violet. The divisions occur with approximate constancy near the wave lengths .65μ and .50μ, which also is the case in Allen's curves.

III. FATIGUE CURVES

In Allen's investigations it was found that when the right eye was fatigued with the primary colors red, green, and violet, one elevation was formed in the corresponding part of the curve, and two reflex depressions in the parts corresponding to the remaining sensations. But when the compound colors, orange, yellow, and blue were used, two

TABLE 3. *Fatigue Curves*

λ	Normal	White Light	Darkness	Darkness and Pressure	.687μ
	sec.	sec.	sec.	sec.	sec.
.74μ	0.0386	0.0440	0.0420	0.0440	0.0485
.72	.0316	.0328	.0355	.0372	.0396
.70	.0266	.0275	.0295	.0316	.0316
.68	.0228	.0243	.0237	.0253	.0265
.66	.0182	.0197	.0200	.0200	.0205
.64	.0161	.0165	.0172	.0169	.0170
.62	.0146	.0154	.0147	.0148	.0157
.59	.0132	.0143	.0136	.0140	.0141
.57	.0130	.0141	.0134	.0138	.0141
.55	.0133	.0147	.0136	.0138	.0140
.53	.0137	.0150	.0137	.0140	.0148
.50	.0163	.0160	.0165	.0161	.0170
.48	.0194	.0187	.0187	.0190	.0202
.46	.0234	.0225	.0215	.0230	.0252
.44	.0295	.0297	.0269	.0304	.0306
.42	.0401	.0428	.0366	.0422	.0635
λ	.660μ	.589μ	.540μ	.450μ	.410μ
	sec.	sec.	sec.	sec.	sec.
.74μ	0.0425	0.0396	0.0396	0.0442	0.0390
.72	.0360	.0330	.0350	.0392	.0313
.70	.0297	.0276	.0300	.0329	.0270
.68	.0254	.0238	.0239	.0275	.0223
.66	.0197	.0196	.0193	.0218	.0186
.64	.0170	.0165	.0169	.0173	.0162
.62	.0152	.0144	.0155	.0151	.0144
.59	.0140	.0135	.0139	.0141	.0135
.57	.0138	.0131	.0137	.0141	.0132
.55	.0145	.0136	.0140	.0140	.0133
.53	.0147	.0143	.0143	.0151	.0138
.50	.0168	.0166	.0173	.0173	.0162
.48	.0200	.0196	.0194	.0210	.0191
.46	.0241	.0240	.0232	.0241	.0245
.44	.0305	.0305	.0300	.0320	.0315
.42	.0503	.0465	.0423	.0495	.0430

elevations were formed with each, corresponding in position to the two sensations directly affected, and a reflex depression in the remaining sensation. Yellow, for example, fatigues both the red and the green sensations, causing corresponding elevations in the curve, and enhances the violet sensation causing a depression.

The assumption of Helmholtz that all colors directly stimulate all three sensations, though in unequal amounts, was confirmed experimentally by the former investigations, and is most emphatically confirmed by the fatigue curves now to be described. In the normal eye there are always opposite effects produced upon the sensations directly

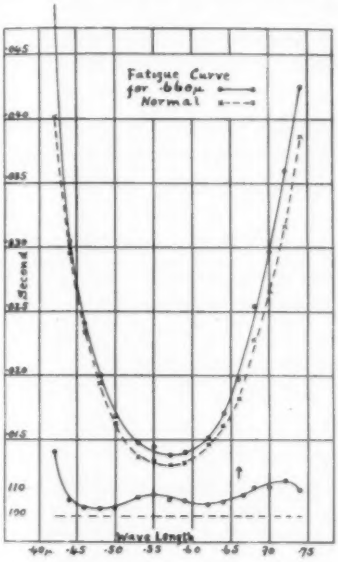

FIG. 6. *Fatigue curve for .660μ.*

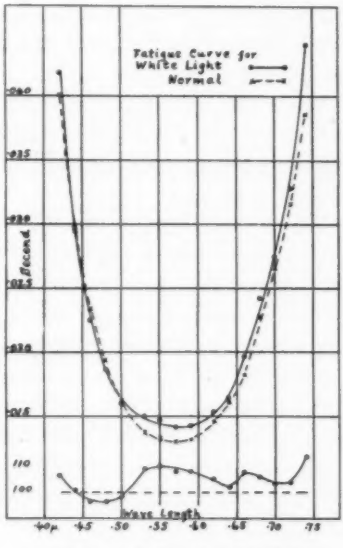

FIG. 7. *Fatigue for white light.*

and those reflexly affected. The two portions of the spectrum thus oppositely influenced are complementary to each other. It will be remembered that these experiments were likewise conducted in a lighted room so that the unused eye was maintained constantly in daylight adaptation.

In the fatigue curves of the writer much the same type of curve is obtained with all the colors used: .687μ, .660μ, .589μ, .540μ, .450μ, and .410μ. The data for these curves are in Table 3, and the curves are similar to that in Fig. 6, for .660μ. It will be noticed at once, especially

in Fig. 9 where all the reduced fatigue curves are shown together, that each curve, with the exception of that for the violet color .410μ, is characterised by three elevations in the parts corresponding to red, green-yellow, and violet, the divisions occurring near the same wave lengths as before, .65μ and .50μ. No depression occurs with any of the colors. With the wave length .540μ, the violet elevation is small, while in the case of violet, .410μ, there is an elevation corresponding to that color, and the rest of the curve is almost coincident with the normal. This suggests that this color is not far from an equilibrium point.

When the eye was fatigued with white light, it was found that the curve in Fig. 7 was elevated above the normal, and possessed three elevations. This clearly shows that white light affects the three sensations red, green, and violet.

When the right eye was blindfolded, or in darkness adaptation, the curve shown in Fig. 8 was obtained. This has a depression in the violet region, whereas Allen found his curve to lie above the normal in all parts.

When pressure upon the eye was added to darkness adaptation the writer found that the violet part of the curve was elevated. The three-fold character of the sensations is again clearly demonstrated.

The reduced curves for white light and darkness are also shown in Fig. 9 with the reduced fatigue curves for the various colors.

From the study of the curves for fatigue or the direct action of light, the conclusion is obvious that all colors affect the three fundamental color sensations directly, in accordance with the assumption of Helmholtz. It is also evident that no reflex effects are shown at all. This does not necessarily mean that no visual sensory reflexes exist, but that the direct effects greatly predominate over them.

The identical three-fold character of the curves for white light and darkness constitutes the strongest evidence that these influences act upon the color sensations, and not upon a separate white-black visual substance or sensation as the Hering theory, for example, assumes.

IV. THEORETICAL CONSIDERATIONS

In the study of color blindness it is frequently stated that one or more sensations, or the corresponding photochemical substances, are absent from the retina. Since in color blindness the spectrum is but little shorter than in normal vision, the conclusion must follow that in addition to the color sensations there is a white process also which is

responsive to all colors. If, however, all colors stimulate all three primary sensations, in accordance with the trichromatic theory, whiteness is fully accounted for without an additional sensation. Since the evidence adduced in this paper is clear and explicit that all colors act upon all three sensations, the assumption (and it must be remembered that in all theories of Color Vision it is only an assumption) of a separate white sensation or process is needless.

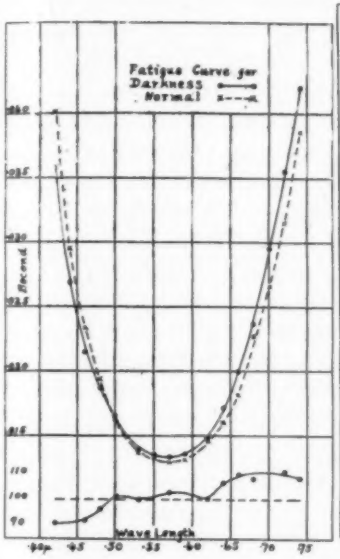

FIG. 8. *Fatigue curve for darkness.*

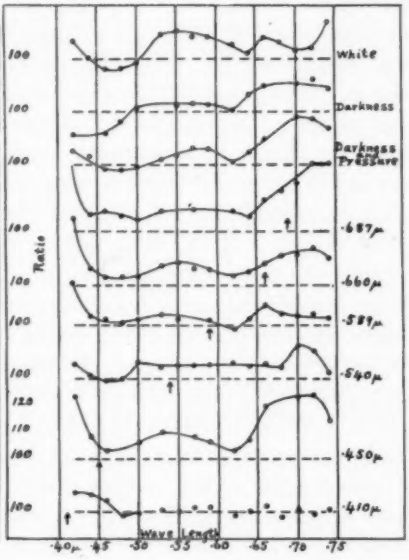

FIG. 9. *Reduced fatigue curves.*

There is no doubt that the writer is defective in his color sense, or is color blind in the usual terminology. It is obvious from the curves that the same three regions are affected as in normal eyes. The conclusion therefore follows that in the writer's eye, three color sensations exist and operate. None are missing. But the abnormal occurrence of the elevations and depressions and the complete absence of the latter in the case of fatigue or the direct action of light, show that in color defectiveness or blindness it is the visual reflexes which are chiefly at fault. Hence when light falls upon the eye the counteracting process to fatigue is too small to be effective, though the reflex curves show it is not entirely absent. Though the writer is red-green blind in the ordinary sense, yet what he considers to be a red color is perceived after pro-

longed fixation, if it is quite bright. Also what he calls a greenish image is formed by successive contrast upon looking at a white surface after fatigue with bright red light.

The writer has never been able to obtain any negative after-images either with color or with white light of the strongest character. Even after looking at a bright electric light, no after-images are seen on closing the eyes, except a positive image of the same color for a very brief time. Allen has previously suggested that negative after-images are due to reflex discharges in the efferent nerves, and that positive after-images are due to the persistence of afferent nerve stimulation. The fact that the writer obtained persistency curves at all is evidence that positive after-images are formed in his eyes. But the absence of negative after-images seems to be significantly connected with the absence of reflex effects in the directly stimulated eye. The curves and other characteristics of vision of the writer are all consistent with each other, though they are not normal except as regards the violet sensation.

Since the three sensations are acted upon in two ways, direct and reflex, it might be inferred that innumerable types of color blindness or deficiency should exist. Allen found, as shown in his paper on color blindness previously referred to, that the normal curves of twenty six cases could be readily classified into seven types, to one of which the writer, as shown by his curve in Fig. 1, belongs. The reflex and fatigue curves for several subjects of each type should now be obtained in order to secure sufficient information for a more thorough understanding of these important peculiarities of vision. While generalisation from a single case of color deficiency is perilous, yet it is evident that the curves do give exact information quite consistent with other facts of defective color vision. There appears to be nothing in these experimental results inconsistent with the trichromatic theory of Young-Helmholtz when enlarged by the addition of the visual sensory reflexes. Or we may say positively that the three-fold character of the curves is quite in harmony with that theory of color vision, and indeed strongly confirms it.

These curves show that defective color vision largely arises from disturbances in the efferent fibres of the reflex arc, which suppress the enhancing reflex actions which are essential to normal color vision. In other words, the various types of color blindness are due to inhibitory processes of abnormally large magnitudes acting selectively upon the visual receptors.

This investigation forms part of a series of researches in Color Vision conducted in the Department of Physics of the University of Manitoba

with the financial assistance of the Honorary Advisory Council for Scientific and Industrial Research, Ottawa.

I desire to record my thanks to Professor Frank Allen, Director of the Department of Physics, University of Manitoba, for suggestions regarding the interpretation of the curves obtained in this investigation.

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UNIVERSITY OF MANITOBA,
WINNIPEG, CANADA.

The Quantum Theory.—By E. P. Adams. 2nd edition, revised and enlarged. Bulletin of the National Research Council, *7*, Part 3, No. 39. Nov. 1923. 109 pp. $1.50.

In writing a second edition of "The Quantum Theory," made necessary by the unusual popularity and consequent exhaustion of the first issue, Prof. Adams has more than amply justified the use of the term "revised and enlarged." Much new material has been added, and the original subject matter has been largely rearranged. In the new edition more emphasis is very wisely placed on the "first" or "stationary state" form of the quantum theory, for the success of the Bohr atom appears to demand very definitely this version of quanta rather than the "second" or "cell" theory. Therefore many texts now almost entirely overlook the latter. Historical and alternative developments, however, should never be completely forgotten, and fortunately in Prof. Adams' book a little space is still retained for acquainting us with the general point of view of the "cell" theory.

In Chapter i, entitled "general dynamical theory," a large number of dynamical principles are assembled,—a rather more involved collection, in our opinion, than is required for an understanding of the quantum theory. An unusual feature is the frequent use of integral invariants. In section 16 a calculus of variations proof, resembling in a general way an early derivation by Ehrenfest, is included of the adiabatic invariance of the quantum condition $2\bar{T}=nh\nu$ for simply periodic systems. A reference is given to Burgers' first method of establishing the generalization of the principle of adiabatic transformability for multiply periodic systems, but no mention is made of Burgers' second derivation, which is reproduced in an appendix of Sommerfeld's "Atombau," and which in our opinion furnishes a much simpler way of proving the invariance of the quantum conditions once the transformation theory of dynamics has been developed. A particularly well chosen section is no. 17, which summarizes Flamm's compact and simple derivation of the number of vibration frequencies of a continuous medium.

Chapter ii opens with a resumé of classical statistical mechanics, and the quantum theory modifications are introduced by way of contrast on following pages. At the end of the chapter Einstein's derivation of the Planck radiation formula is given. This is so exceed-

ingly simple and fundamental that it should be inserted in every text on the quantum theory, but books in which it is included are the exception rather than the rule.

Chapters iii and iv deal largely with the specific heats of solids and gases, and the calculation of the absolute value of the entropy. These chapters are perhaps the most interesting and valuable part of the entire bulletin. Especially is this statement true because few good English texts are available on these phases of the quantum theory (Reiche's book is an exception). Excellent judgment is shown in including only the analyses of specific heats based on the most modern forms of the quantum theory, and therefore omitting the many historical attempts which must now be regarded as gropings in the dark before definite ideas of the quantum conditions had been evolved. The inclusion of section 31 on the quantization of a non-linear oscillator is of interest not only because of its bearing on the increase in specific heats above the equipartition value at high temperatures, but also because it is illustrative of the perturbation theory technique developed by Born and his associates.

Chapter v is devoted mostly to the spectrum of hydrogen and ionized helium. The Stark effect and relativity corrections are treated after the customary, rather formal, separation of variables method. An unusually complete comparison is given of the observed and computed frequency differences in the Stark effect. Prof. Adams is to be commended for including so much of Kramers' theoretical work on the intensities of Stark effect components, which is a most striking confirmation of the correspondence principle, but which is given insufficient space and emphasis in most texts. The Zeeman effect is treated by Debye's method, now too often overlooked.

Chapter vi commences with a useful synopsis of photoelectric and allied phenomena, and then passes on to a discussion of Whittaker's interesting magnetic wheel atomic model for the photoelectric absorption and emission of quanta. In Chapter vii some of Allen's work on the magneton is given, in addition to a resumé of the experiments of Stern and Gerlach.

In conclusion, we may say that many important and diversified applications of the quantum theory are summarized in Prof. Adams' bulletin. The chief criticism that might be made is that the mathematical analysis leading to the quantum conditions is made to appear rather too formidable. Except, however, for the writings of Bohr, this fault is common to practically all texts, which in deriving the quantum conditions and energy formulae almost invariably emphasize what Campbell aptly terms "the separation of variables apparatus" at the expense of the correspondence principle and the theorem of mechanical transformability (adiabatic invariance),—the two great beacon lights for the yet untravelled way which will ultimately join together the classical and quantum mechanisms of radiation.

J. H. VAN VLECK

TABLE——*Values of Relative Visibility.*

Wave Length in Milli-microns	V_1	V_2	Σ V_1+V_2	Transmission. Ives' Physical Photometer Solution	V_3	Σ $V_1+V_2+V_3$	V_4	Σ $V_1+V_2+V_3+V_4$	Visibility, Recommended, Gibson and Tyndall.	Visibility, Equation, Tyndall and Gibson.
430	0.00081		0.00081			0.00081		0.00081	0.0116	0.0008
440	.0029		.0029			.0029	0.0120	.0149	.023	.015
450	.0055		.0055			.0055	.0241	.0296	.038	.030
460	.0232		.0232	0.007		.0232	.0348	.0580	.060	.058
470	.0531		.0531	.029		.0531	.0369	.0900	.091	.090
480	.1080		.1080	.091		.1080	.0297	.1377	.139	.138
490	.1959		.1959	.185	0.0009	.1968	.0184	.2152	.208	.215
500	.3202		.3202	.317	.0083	.3285	.0090	.3375	.323	.337
510	.4744		.4744	.478	.0350	.5094		.5094	.503	.509
520	.6414		.6414	.652	.0624	.7038		.7038	.710	.704
530	.7973		.7973	.799	.0535	.8508		.8508	.862	.851
540	.9173	0.0016	.9189	.911	.0236	.9425		.9425	.954	.943
550	.9815	.0052	.9867	.985	.0053	.9920		.9920	.995	.992
555	.9896	.0085	.9981		.0020	1.0001		1.0001	1.000	1.000
560	.9817	.0131	.9848	.999		.9848		.9848	.995	.985
570	.9222	.0271	.9493	.957		.9493		.9493	.952	.949
580	.8174	.0459	.8633	.888		.8633		.8633	.870	.863
590	.6861	.0655	.7516	.782		.7516		.7516	.757	.752
600	.5474	.0788	.6262	.639		.6262		.6262	.631	.626
610	.4166	.0818	.4984	.494		.4984		.4984	.503	.498
620	.3033	.0723	.3756	.365		.3756		.3756	.381	.376
630	.2120	.0562	.2682	.261		.2682		.2682	.265	.268
640	.1426	.0383	.1809	.170		.1809		.1809	.175	.181
650	.0925	.0231	.1156	.094		.1156		.1156	.107	.116
660	.0581	.0126	.0707	.051		.0707		.0707	.061	.071
670	.0353	.0061	.0414	.029		.0414		.0414	.032	.041
680	.0209	.0027	.0236	.014		.0236		.0236	.017	.024
690	.01198		.01198	.008		.01198		.01198	.0082	.0120
700	.00671		.00671			.00671		.00671	.0041	.0067
710	.00367		.00367			.00367		.00367	.0021	.0037
720	.001962		.001962			.001962		.001962	.00105	.0020

$$V_1 = 0.9896\ (R_1 e^{1-R_1})^{200} \qquad R_1 = \frac{555}{\lambda}.$$

$$V_2 = 0.0820\ (R_2 e^{1-R_2})^{550} \qquad R_2 = \frac{607}{\lambda}.$$

$$V_3 = 0.0650\ (R_3 e^{1-R_3})^{2000} \qquad R_3 = \frac{523}{\lambda}.$$

$$V_4 = 0.0375\ (R_4 e^{1-R_4})^{430} \qquad R_4 = \frac{467}{\lambda}.$$

VISIBILITY OF RADIANT ENERGY EQUATION

By E. P. T. Tyndall and K. S. Gibson

Various empirical relations have been formulated to express mathematically the relative visibility of radiant energy, each equation being fitted to some certain experimental determination. In a recent paper[1] the writers recommended a set of average visibility data based on their own and previous determinations. An equation to express this recommended average has obvious uses. A formula, similar to the one proposed by Kingsbury,[2] is found to fit very closely. The visibility at any wave-length, V_λ, is the sum of several terms, V_1, V_2, V_3, V_4, etc., the number depending on how closely and over what range it is desired to reproduce the experimental data.

The following 4-term expression has been derived:

$$V_\lambda = 0.9896\,(R_1 e^{1-R_1})^{200} + 0.0820(R_2 e^{1-R_2})^{550} + 0.0650(R_3 e^{1-R_3})^{2000} + 0.0375\,(R_4 e^{1-R_4})^{620},$$

where $$R_1 = \frac{555}{\lambda}, \quad R_2 = \frac{607}{\lambda}, \quad R_3 = \frac{523}{\lambda}, \text{ and } R_4 = \frac{467}{\lambda}.$$

In the accompanying table are given the computed values of the separate terms for every 10 millimicrons and the summation of two, three, and four terms. For comparison with the sum of V_1 and V_2 is given the transmission of Ives' physical photometer solution.[3] It is interesting to note the agreement. The accuracy with which the formula represents the experimental facts is shown by comparing the last two columns of the table.

The writers wish to express their indebtedness to Mr. H. J. Keegan for making the computations.

State University of Iowa (E.P.T.T.)
National Bureau of Standards (K.S.G.)
May, 1924.

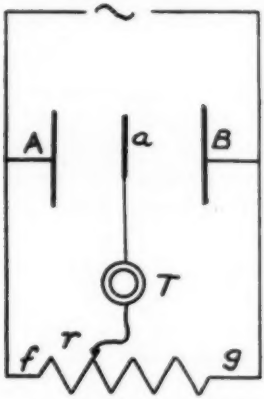
Comparison of Energy Absorbed by a Fluorescent Dye-solution with Energy Re-radiated in Fluorescence.—The brightness of a dilute fluorescing solution was compared photometrically with the brightness of a matt surface illuminated by the exciting light, Lambert's law being postulated for the latter surface and Lommel's (equal intensity

[1] B. S. Sci. Pap. No. 475, p. 174; 1923. Cf. also Trans. I. E. S., *19*, p. 176; 1924.
[2] Phys. Rev. (2), 7, p. 161; 1916.
[3] Jour. Frank. Inst., *188*, p. 218; 1919.

of radiation in all directions) for the solution. The absorption was separately determined by a conventional method. All the measurements were made at various wave lengths of the light obtained from a filament lamp, and the final values for absorbed energy and re-radiated energy are integrals over the spectrum. The values are admittedly quite inexact. For ten different dye-solutions the "fluorescent efficiency" (ratio of re-radiated to absorbed energy) ranges between 80% to a vanishingly small value. The fluorescence bands are steep towards short waves and less so towards long waves, and their maxima are in every case about 23 mμ towards long waves from the maxima of the absorption bands.—[S. J. Wawilow, Moscow; ZS. f. Phys., *22*, pp. 262-272; 1924.]

K. K. DARROW

On a Method of Exploring Alternating Electrostatic Fields.—This method of exploring electrostatic fields is illustrated by the figure for a simple case. An alternating difference of potential is maintained across the plates *A* and *B*, the field between which it is desired to determine. The "probe," *a*, is located on the equipotential surface whose potential is to be measured and is connected through a detector of alternating currents, *T*, to the sliding contact of the slidewire *fg*. Absence of current through *T* indicates the equality of the



potentials at *a* and at *r*, the latter of which is known from the position of the brush. In order to prevent the charging current of the conductor between *a T* from affecting the results, it is surrounded by and insulated from a conductor which is attached to the brush *r*. The use of the method is illustrated by an investigation of the field in and about an irregularly shaped petticoat insulator. A precision of setting of one per cent is apparently readily attainable. [Semenoff and Walther, ZS. f. Physik *19*, pp. 136-40, 1923.]

L. BEHR

SPECTRA OF LUMINESCENCE OF GRIGNARD COMPOUNDS

By R. T. Dufford, Dorothy Nightingale, and S. Calvert

Elsewhere[1] the writers have described the results of an extended investigation of the luminescence of compounds of the type RMgX, where R is an organic radical, and X a halogen. These compounds (known as Grignard compounds) are generally not themselves fluorescent. But if the magnesium is attached directly to an unsaturated carbon atom in R, and especially if R is an aromatic radical, these compounds radiate visible light when oxidized with O_2, i. e., they are

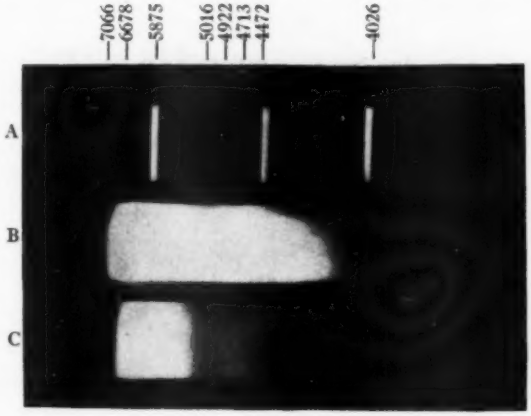


Fig. 1. *(A) Spectrum of helium; (B) Spectrum of light from Schwersenski and Caro reaction; (C) Spectrum of white light.*

chemi-luminescent, often brightly so. In the process of oxidation, unstable products are formed, probably of the type ROMgX, which are generally quite strongly fluorescent in ultraviolet light.

Certain writers have stated that in such cases as this, where chemi-luminescence occurs in the formation of a product, and the product itself is photo-luminescent, the two radiations are alike in spectral distribution of energy, and probably are due to the same radiating mechanism. For example, Zocher and Kautsky,[2] after discussing a number of

[1] Dufford, Calvert and Nightingale, J. Am. Chem. Soc. *45*, p. 2058; 1923.
[2] Zocher and Kautsky, ZS. fur Elektrochemie *29*, p. 308, 1923.

such cases, arrive at that conclusion, and cite only an observation by one of the writers[3] as evidence to the contrary.

However, while the fluorescence spectra are bright enough to be studied without extreme difficulty, the chemi-luminescence spectra are less easy. Indeed, photographs of such spectra are practically absent from the literature. The picture by Ives and Coblentz[4] of the spectrum

FIG. 2. *(A) Helium spectrum; (B) Chemi-luminescence spectrum from oxidation of (1, 4) $ClC_{10}H_6MgBr$.*

of the light from a firefly, seems to be the only case where a chemi-luminescence spectrum has been published; though Forsythe[5] records having obtained such a spectrum of light from luminescent bacteria, using an especially-built spectrograph. Apparently no spectra of light

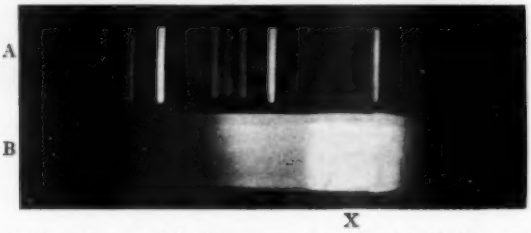


FIG. 3. *(A) Helium spectrum; (B) Fluorescence spectrum of oxidation product of (1, 4) $ClC_{10}H_6MgBr$. (X) Spectrum of exciting light.*

from synthetic substances, that can be prepared at will in the laboratory, have been published. The reason is simply that the surface brightness of these compounds is so low, being at best only a few milliamberts,

[3] Evans and Dufford, J. Am. Chem. Soc. *45*, p. 278, 1923.

[4] Ives and Coblentz, U. S. Bur. Stds., Bull., *6*, p. 321; 1909.

[5] Forsythe, Nature, *83*, p. 7; 1910.

often less, that no ordinary spectrograph will photograph their spectra, even with unreasonably long exposures. Hence most workers investigating such luminescence spectra have been driven to the use of indirect methods, such as, for example, the use of color-filters.

It seemed of interest, therefore, to record the results of some direct spectrum photographs of chemi-luminescence, which the writers obtained during the past year, and also to describe the method used, since it may be of value in other cases where very faint spectra are to be dealt with.

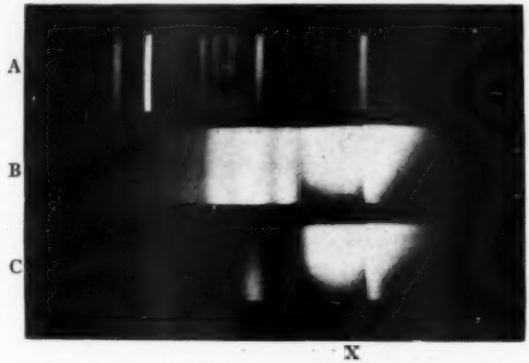


FIG. 4. *(A) Helium spectrum; (B) Fluorescence spectrum from oxidation product of p-ClC$_6$H$_4$MgBr; (C) Fluorescence spectrum from oxidation product of p-BrC$_6$H$_4$MgBr. (X) Spectrum of exciting light.*

Obviously, the problem is simply that of obtaining an instrument of sufficiently high aperture-ratio. Fortunately, the writers had available a large glass prism made by Petitdidier, with edges about three inches. For lenses to go with this prism, two objectives from opaque projectors were used. These had focal lengths of about 40 cm, and were wide enough to utilize the full aperture of the prism. When suitably mounted in boxes, with plate-holder and slit, the combination proved to be an instrument of gratifying speed. The spectrum of the capillary of a helium tube of H form, viewed sidewise, could be photographed on an ordinary panchromatic plate in one second, and any ordinary fluorescence spectrum in less than an hour, often less than half that. The exposures for the chemi-luminescence spectra, however, ranged from three to twelve hours, except in one case.

The chemi-luminescence spectra obtained all verify the result of previous visual observations, in that they all prove to be continuous,

without structure. The first spectrum shown is that of the interesting reaction of Schwersenski and Caro.[6] In this reaction, concentrated sulphuric acid acts on small crystals of potassium permanganate in a test-tube, small bubbles of gass being evolved. On rising into a supernatant layer of formaldehyde (or alcohol), each bubble causes a bright

FIG. 5. *(A) Helium spectrum; (B) Chemi-luminescence spectrum from oxidation of* p-BrC_6H_4MgBr.

flash of yellowish light. The light is therefore intermittent, and hence it is difficult to estimate its intensity; but it is so bright that an hour of this intermittent exposure gave the picture shown. For comparison, the spectrum of helium, and the spectrum of a carbon glow lamp, are given; the latter illustrates the effect of the sensitivity curve of the plate in producing an apparent minimum in the green.

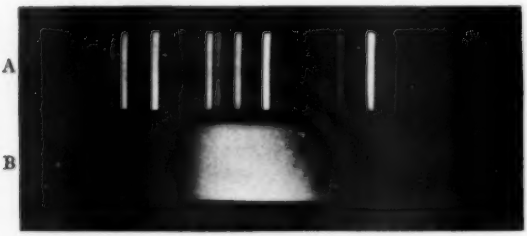


FIG. 6. *(A) Helium spectrum; (B) Chemi-luminescence spectrum from oxidation of* p-ClC_6H_4MgBr.

The remaining spectra deal with Grignard compounds. First are two spectra from a naphthalene derivative, $(1.4)ClC_{10}H_6MgBr$, showing the chemi-luminescence during oxidation, and the fluorescence of the oxidation product, respectively. The fluorescence spectra from naphthalene

[6] Schwersenski and Caro, Chem. Ztg. *22*, p. 58; 1898.

derivatives generally show a single band, which is not, however, quite identical with the chemi-luminescence band. But even if it were quite so, that would not necessarily prove the identity of the radiating mechanisms; for it is easy to cite cases of closely similar luminescence spectra from very different sources.

The last two pairs of spectra show the chemi-luminescence and the fluorescence associated with the compounds $p-BrC_6H_4MgBr$ and $p-ClC_6H_4MgBr$, respectively. This last compound is of considerable interest on account of the unusual brightness of the light it gives out. It will be seen that these fluorescence spectra are clearly multiple-banded, while the chemi-luminescence spectra show but one band, thus demonstrating clearly that the phenomena are not identical.

PHYSICAL AND CHEMICAL LABORATORIES,
THE UNIVERSITY OF MISSOURI,
JUNE 1, 1924.

Isotope Effects in the Band Spectra of Boron Monoxide and Silicon Nitride.—"Every one of the approximately 80 bands of $B^{11}O$, including those both of the α and of the β systems, is matched, so far as can be determined, by a corresponding $B^{10}0$ band of about the expected intensity (2/9 that of the $B^{11}O$ bands). In each system, the central band, corresponding to an electronic change alone in a vibrationless molecule, is practically coincident for the two isotopes. From this center the bands extend both toward lower and toward higher frequencies, the pattern being exactly the same for both isotopes; the scale or spacing of this pattern, however, being larger for the lighter isotope in a ratio approximately equal to the ratio of the molecular vibration frequencies. . . . The maximum separation between corresponding bands . . . is more than 300 wave number units in each system (this amounts to about 200 A near λ 8500 in the α-system). Quantitatively the theoretical value of ρ (ratio of frequencies $B^{10}0/B^{11}O$) is 1.0276 for BN and 1.0292 for BO. The average experimental value from measurements on the β system is 1.0283 for the initial electronic state of the molecule and 1.0294 for the final state, the latter figure being much more trustworthy than the former." Furthermore the spacings of the lines in individual bands stand, in the two families, approximately as ρ^2 (i.e. inversely as the moment of inertia). The quantitative agreement in this case is far better when the molecule is assumed to be BO, as in the title of this paper, than if it is assumed to be BN, as originally. With silicon nitride there are 3 families of bands, two much feebler than the third; there is excellent quantitative agreement with the assumption that they are due to $Si^{29}N$ and $Si^{30}N$, which are apparently about 2% as abundant as $Si^{28}N$ to judge from the atomic weight. [R. S. Mulliken, Harvard, Nature *113*, pp. 423-424; 1924.]

K. K. DARROW

EDITORIAL

Reports from the National Research Council.

In this issue appears the first of a series of reports prepared for, and by request of, the Committee on Research Methods and Technique of the Division of Physical Sciences of the National Research Council. The reports are written by specialists, and are intended, not as a text-book like exposition of the several subjects, but rather as brief summaries in such form, that, by aid of the references given, an investigator, or student, starting in a field new to him may familiarize himself with the various methods of measurement and may select the method most suitable for the particular problem. It is hoped that the articles will prove useful to the investigator in college or industrial laboratory, to the advanced student of physics, and to investigators in allied sciences who employ physical methods of research. Each report gives a reasonably complete survey of the subject treated, but is not necessarily exhaustive.

The National Research Council has made these reports available for publication in this Journal. On behalf of our readers we wish to express to the Council our appreciation of this courtesy, and to the authors of the several reports we wish to extend our thanks for their painstaking efforts.

It is hoped that, when the publication of the series as now prepared, is completed, other similar reports may from time to time be presented. The Editors welcome suggestions.

The Committee on Research Methods and Technique comprises F. K. Richtmyer, Cornell University, Chairman; L. J. Briggs, Bureau of Standards; A. D. Cole, Ohio State University; H. B. Lenson, University of Chicago; R. S. Minor, University of California; J. R. Roebuck, University of Wisconsin; H. B. Williams, Columbia University.

EDITORS.

INSTRUMENT SECTION

THE PRODUCTION OF COLD*

By C. W. Kanolt

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The methods of producing cold that have found practical application, and some that have been proposed but never utilized, are presented in the following list.

* Published by permission of the Director of the Bureau of Standards, of the U. S. Department of Commerce.

One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of physical measurements. See Editorial in this Journal 9, p. 410, 1924.

1. The absorption of heat as latent heat, including heat of vaporization, heat of fusion and heat of solution.

2. The cooling of a fluid by the doing of mechanical work in expansion against a moving mechanism.

3. The Joule-Thomson effect.

4. The conversion of heat energy into kinetic energy of flow.

5. The cooling of a fluid by the doing of work in expansion against an electric force.

6. Cooling by chemical action.

7. The Peltier cooling.

All but the last two of these will be treated in some detail in the following sections.

An example of cooling by chemical action without the influence of latent heats is afforded by a mixture of ammonium chloride and potassium nitrate in the form of powders, in the presence of a trace of moisture. A mixture of concentrated hydrochloric acid and hydrated sodium sulphate has been employed as a freezing mixture.[1] In this case the cooling is produced only in part by chemical action.

The Peltier cooling is produced when an electric current is passed in the proper direction through a junction between two different metals. Under ordinary conditions difficulties in using this as a source of cold would be presented by the generation of heat as the result of resistance, and by the conduction of heat by the metals. The method has never been employed in practice.[2]

FREEZING MIXTURES.—A freezing mixture can be made from a solid and a liquid, from two liquids, or from two solids, forming a liquid solution. Heat is absorbed to supply the heat of fusion or the heat of solution or both. The distinction made between the influence of heat of fusion and that of heat of solution is somewhat arbitrary. For example, when ice and common salt are mixed the process may be properly considered as consisting of the dissolving of both salt and ice in a salt solution, and from this point of view two heats of solution are involved; but if the process consisted of first the melting of the ice and then the solution of the salt in the water the amount of heat absorbed would be the same, provided the final temperature was the same, yet the latent heats involved would be the heat of fusion of ice and the heat of solution of salt.

[1] Szydlowski, Akad. Wiss. Wien. Ber., *116*, 2a, pp. 855-891; 1907.

[2] Relative to its suggested use at extremely low temperatures see Martin, Nature, *64*, p. 376; 1901, Chem. News, *84*, p. 73; 1901, Nature, *107*, p. 43; 1921; Swinton, Nature, *106*, p. 828; 1921.

The most common freezing mixtures are those composed of ice with some soluble solid, usually a salt. A mixture of a suitable salt with water may be used as a cooling agent, but if a large absorption of heat is desired much is to be gained by using dry ice and a salt that has already been cooled to 0° by ice, for this has the advantage of beginning the process at 0° and especially of making the large absorption of heat in the melting of ice available. If ice is used, the other substance may be one which produces little or no cooling by solution but has a high solubility and hence can produce solutions of low freezing point, the cooling resulting mostly from the melting of the ice.

If the salt can be obtained both with and without water of crystallization, the hydrated form should usually be used, if it is available, because the formation of a hydrated salt from an anhydrous one usually involves the evolution of heat, so that more cooling can be obtained by dissolving the hydrated salt. Most hydrated salts dissolve with absorption of heat, while many anhydrous salts dissolve with evolution of heat. In the case of sodium chloride, the hydrated form, $NaCl.2H_2O$, is unstable at ordinary temperatures. Calcium chloride should be used in the form of $CaCl_26H_2O$, which is sold as "crystallized calcium chloride."

If the lowest obtainable temperature is desired, together with the maximum absorption of heat, the materials should be mixed in the proportions to form the eutectic, the mixture having the lowest freezing point. Mixtures in quite different proportions may be capable of producing the eutectic temperature but the heat they can absorb per unit mass will be less. Eutectic mixtures of salts and water are called cryohydrates. A solution of this composition can exist in equilibrium with both ice and the salt at its freezing point. If ice and a salt are mixed in the eutectic proportions, a solution will be formed with absorption of heat until either all the material has entered the solution or it has all been reduced to the eutectic temperature. With most freezing mixtures that start with ice at 0°, the absorption of heat is more than the amount necessary to reach the eutectic temperature if no heat is taken from other bodies. An exception to this is presented by diluted sulphuric acid and ice.

If the temperature required is above the eutectic temperature other proportions of ice and salt than the eutectic will give more cooling for a given mass of the mixture. Let us calculate how much heat a mixture will have absorbed at a given temperature when all the ice is melted and all the salt dissolved, and then find what mixture will absorb the greatest quantity.

Let s represent the fraction of the mixture that is salt, $-t^\circ$ the temperature centigrade to be reached, C_i and C_s the mean specific heats of ice and of the salt between 0° and $-t^\circ$, Q_i the heat absorbed by the fusion of a unit mass of ice at 0°, Q_s the heat evolved by the solution of unit mass of the salt at $-t^\circ$. Since the external work involved in the processes of fusion and solution at atmospheric pressure is negligible, the net amount of heat absorbed will be independent of the order of these processes. Suppose for the purpose of calculation that first the ice is melted, then the water and the salt are cooled to $-t^\circ$ without freezing of the water and then the salt is dissolved. The heat absorbed by the fusion of the ice and the solution of the salt, per unit mass of the mixture, will be

$$(1-s)Q_i-sQ_s$$

The part of this employed in cooling the material is

$$t[sC_s+(1-s)]$$

if variation in the specific heat of water with temperature is neglected. The heat that can be absorbed from other bodies is the difference between these, which is

$$L=Q_i-t+(-Q_i-Q_s-C_st+t)s$$

The coefficient of s, in which $-Q_i$, $-C_st$ and sometimes $-Q_s$ are negative, is usually or always negative, owing mainly to the large value of Q_i. Hence the largest value of L corresponds to the smallest possible value of s, which is determined by the condition that the freezing point of the solution must not be above the temperature required. Hence to absorb at a given temperature the maximum amount of heat per unit mass of freezing mixture the proportions of ice and the other cooling agent should be those of a solution, the freezing point of which is the required temperature.

The compositions of some such solutions are shown in Table 1, with the eutectic compositions and temperatures. While these data may not all be very accurate, they can be used as a guide in selecting a suitable mixture for a given purpose. The last column in this table gives the quantity of heat that can be absorbed at the temperature given in the second column by one gram of freezing materials which had before mixing the temperature of 0°C.

This table shows that sodium chloride and ammonium nitrate are the most effective materials for temperatures above their eutectic points, while for temperatures from −55° to −21.2° hydrated calcium

chloride is most effective. Temperatures down to $-75°$ could probably be obtained by using ice and diluted sulphuric acid if both were pre-

TABLE 1.—*Freezing Mixtures*

Material	Temperature Centigrade Degrees	Percentage of Dissolved Material in Solution Freezing at this Temperature		Available Cooling. Gram Calories per Gram of Mixture.
	0	0		79.7[6]
NN_4NO_3	−10	26.5[1]		68[4]
with ice	−17.5[1]	43.3 (eutectic)		57
NaCl	0	0		79.7[6]
with ice	−10	13.4[2]		63[4]
	−20	21.4		49
	−21.2[3]	22.4[3] (eutectic)		47
		(Percentage of $CaCl_26H_2O$)		
$CaCl_26H_2O$	0	0		79.7[6]
with ice	−10	30.0[5]		54[5]
	−20	43.5		42
	−30	50.5		33
	−40	55.0		26
	−50	58.0		20
	−55	58.8 (eutectic)		18
H_2SO_4 solution (66.19%) with ice		Percentage of H_2SO_4	Percentage of 66.19% acid	
	0	0	0	79.7[6]
	−10	16.2[8,9]	24.5	42[7]
	−20	24.0	36.3	21
	−30	28.5	43.1	7
	−37	30.6	46.2	0
	−40	31.2	47.1	
	−50	33.5	50.6	
	−60	35.2	53.2	
	−70	36.7	55.4	
	−75	38.0 (eutectic)	57.4	

[1] Tollinger, Akad. Wiss. Wien, Ber., *72, 2*. p. 535; 1875.
[2] de Coppet, Ann. Chim. Phys., *25*, p. 511; 1872.
[3] Gröber, Dissertation, München; 1908.
[4] Estimated from other data.
[5] Hammerl, Akad. Wiss. Wien. Ber., *78, 2*, p. 59; 1879.
[6] Dickinson and Osborne, Bureau of Standards, Sci. Paper 248; 1915.
[7] Pfaundler, Akad. Wiss. Wien. Ber. *71, 2*, p. 509; 1875.
[8] Pfaundler and Schnegg, Akad. Wiss. Wien. Ber., *71, 2*, p. 351; 1875.
[9] Pickering. Chem. Soc. J., *57*, p. 331; 1897.

viously cooled to a low temperature by a mixture of hydrated calcium chloride and ice.

When the ingredients of a freezing mixture are mixed they do not usually pass into the liquid phase in equivalent amounts during the period before all has become liquid. If the material used with the ice is a liquid, as dilute sulphuric acid, or a solid that dissolves rapidly, the first result of mixing may be the production of a liquid of lower freezing point than the final, and if little heat is absorbed from other objects the temperature may first go below the freezing point of the complete mixture, rising later as the ice is melted by heat taken from other objects.

COOLING WITH SOLID CARBON DIOXIDE.—For the production of temperatures somewhat lower than can be obtained by ice mixtures, carbon dioxide is useful. It is widely available in cylinders containing the liquid under high pressure. It can not exist as a liquid at atmospheric pressure, for its triple point is at 5.11 atmospheres and a temperature of $-56.4°C$.[3] When a cylinder is opened to the atmosphere the material is cooled by vaporization and by the Joule-Thomson effect. If the cylinder is partly inverted so that liquid instead of gas enters the valve, most of the cooling occurs in the escaping material, which is then partly solidified. If a flannel bag is placed over the valve the carbon dioxide snow can be collected. Its sublimation temperature is $-78.5°C$. at a pressure of one atmosphere.[4] Lower temperatures can be produced by applying a vacuum. For instance, at a pressure of 11 millimeters of mercury the temperature is $-122°$.[5]

When solid carbon dioxide is placed in contact with an object to be cooled it vaporizes at the points of contact without the formation of a liquid phase, and an insulating layer of vapor is formed between it and the object. For this reason the transfer of heat is slow. This difficulty is overcome by mixing the snow with a liquid that does not freeze at the temperature reached. Gasoline, alcohol, ether or various other liquids can be used for this purpose. The temperatures produced when these liquids are employed are nearly or quite the same as that obtained without them, though carbon dioxide is of course expended in cooling the liquid.

COOLING BY SPRAYED LIQUID.—Objects may be cooled by applying a volatile liquid in the form of spray and producing cold by its evaporation. For the temporary cooling of small quantities of material or small

[3] Zeleny and Smith, Phys. Zeits., *7*, p. 667; 1906.
[4] Henning, Ann. d. Phys., *43*, *2*, p. 282, 1914.
[5] Zeleny and Smith, loc. cit.

pieces of apparatus the simplicity and convenience of this method may outweigh its lack of economy. Liquids whose boiling points are below ordinary temperature produce the lowest temperatures, in this way, and some of these can be purchased under pressure in cylinders. To obtain liquid from the cylinder it should be inverted and the stream of vapor and sprayed liquid so obtained caused to impinge upon the object to be cooled. In the case of carbon dioxide the liquid is frozen in the stream and it may be preferable to collect the solid carbon dioxide in a bag and employ it as already described. Liquids whose boiling points are above room temperature may be applied by means of an atomizer. A number of suitable liquids, with their boiling points are listed in Table 2.

TABLE 2.

Material	Boiling Point, Centigrade Degrees
Chloroform	61.2
Carbon disulphide	46.2
Ether	34.6
Ethyl chloride	14.
Volatile petroleum distillates	0 to 70
Methyl chloride	−24.1
Nitrous oxide	−89.8

The temperature produced may be much lower than the boiling point, which is only one of the determining factors in the result. Of these materials chloroform and nitrous oxide have the advantage of not being inflammable. The use of an inflammable liquid for this purpose obviously involves a fire hazard.

GENERAL PRINCIPLES OF MECHANICAL COOLING.—The methods of mechanical cooling, including those in which the liquefaction of the refrigerating fluid is the sole object of the process, are so correlated in their thermodynamic principles that it is well first to survey the systems as a whole, with especial reference to the influence of variations in method of operation upon the efficiency, before considering the mechanical details of individual systems. In mechanical cooling cold is produced by the compression and subsequent expansion, under various conditions, of a suitable fluid. The system may be designed solely for the production of cold, as in a refrigerating plant, in which case the choice of the fluid depends largely upon the efficiency obtainable with it. By a refrigerating plant is meant a system in which cold is produced by the use of a fluid which passes repeatedly through a cycle

of operations. On the other hand the purpose may be the cooling of the medium itself in order to liquefy it, or to purify it or for other reasons. The principles and methods employed in the two processes are much the same.

The refrigerating cycle may produce cold by the expenditure of mechanical energy or by the utilization of heat without the intermediation of mechanical energy. The first method is the more often employed and will be considered first. The second will be considered in the section on the absorption system.

The mechanical systems may be classified according to whether the cooling is produced mainly by the vaporization of the liquefied working fluid, by expansion in a cylinder with the performance of mechanical work, or by the Joule-Thomson cooling produced in the expansion of a fluid through a throttle.

THERMODYNAMIC CHARTS.—It is possible to make a complete analysis of any compression refrigerating cycle when the relations connecting the pressure, volume, temperature, entropy and heat content, or "total heat," of the fluid are known. More or less extensive tables of properties are available for the more commonly used refrigerating fluids. The study of a cycle and the calculation of its efficiency are facilitated by the use of charts upon which these quantities are plotted. Since only two of the properties of a particular fluid are independent, all states of the fluid can be represented upon a two-dimensional chart. Among the more important of these are temperature-entropy charts, Mollier heat content charts, and pressure-volume charts. Mollier[6] plotted charts in which heat content and entropy, or heat content and pressure, were used as rectilinear coordinates.

These are especially useful in calculations of performance because two important quantities are measured by changes in heat content, and since in this chart heat content is one of the rectilinear coordinates and is plotted upon a uniform scale, changes in heat content are easily measured. The two quantities mentioned are the heat transfer in expansion or compression at constant pressure, and the net work done in a cylinder in the three operations of drawing in fluid at constant pressure, compressing or expanding it adiabatically to a second pressure, and driving it out at this pressure.

Heat content and entropy have been most often used as coordinates, but more accurate calculations can be made with a chart of a given size

[6] Mollier, Zeits. Vereines Deutsch. Ing., *48*, *1*, p. 271; 1904.

by using pressure, or preferably the logarithm of pressure, in place of entropy, as a coordinate.

The changes of state that occur in a refrigerating cycle are usually changes in each of which some one of the five quantities mentioned remains so nearly constant that variations from this condition can be neglected. In adiabatic expansion or compression in a cylinder the entropy may be treated as constant; in throttle expansion the heat content is constant, provided, as is usually the case, the expansion is so rapid as to be practically adiabatic. Changes at constant pressure and at constant temperature also occur in refrigerating cycles. Such changes are readily followed on a chart by following lines of constant entropy, heat content, pressure or temperature as the case may be.

Mollier diagrams for ammonia, carbon dioxide, and sulphur dioxide will be found in a Report of the Refrigeration Research Committee of the (British) Institution of Mechanical Engineers.[7] The ammonia data in this report are those of Goodenough and Mosher.[8] A somewhat different chart for ammonia is given by Keyes and Brownlee.[9] The most recent ammonia chart is that prepared from determinations at the Bureau of Standards.[10] A table of data on the physical properties of ammonia, carbon dioxide, sulphur dioxide, methyl chloride and ethyl chloride, collected from various sources, can be obtained from the Bureau of Standards. A temperature-entropy chart for air has been prepared by Prof. Harvey N. Davis of Harvard University.

THE CARNOT CYCLE.—Before considering practical refrigerating systems we will first consider what would be a thermodynamically ideal system, and then how such a system must be modified to meet practical conditions.

The coefficient of performance of a refrigerating cycle may be defined as the ratio of the amount of heat energy transferred from the low temperature to the high temperature to the mechanical energy expended. The maximum coefficient of performance would be possessed by an ideal reversed Carnot cycle. In the temperature-entropy chart of Fig. 1, such a cycle is indicated by heavy lines. This chart represents approximately the properties of carbon dioxide. On it are drawn lines of constant pressure, constant heat content and, in the region of mixed liquid and vapor, lines of constant quality, that is, lines upon which the

[7] Inst. Mech. Eng., Proc., p. 645; 1914.
[8] Univ. of Illinois, Eng. Exp. Sta., Bull. No. 66; 1913.
[9] The Thermodynamic Properties of Ammonia, John Wiley & Sons, New York; 1915.
[10] Bureau of Standards Misc. Publ. No. 52; 1923.

proportions of liquid and vapor are constant. The boundary curve, drawn as a heavy line, separates mixed liquid and vapor from liquid on the one side and from superheated vapor on the other. The highest point of this boundary curve is the critical point.

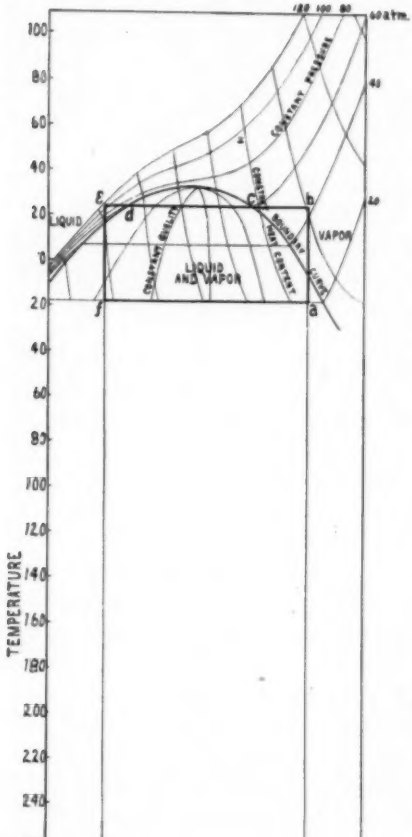

FIG. 1. *Carnot cycle on a temperature-entropy chart.*

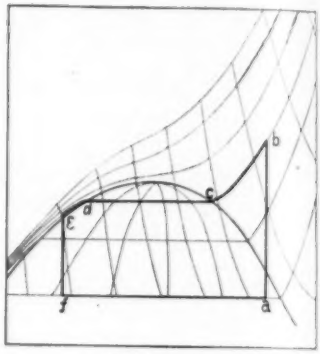

FIG. 2. *Joule cycle.*

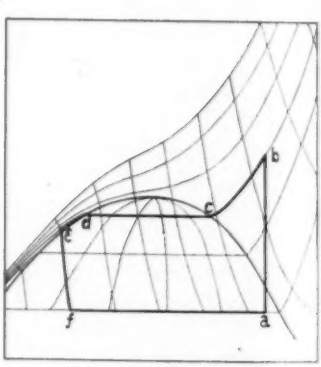

FIG. 3. *Cycle with throttle expansion.*

The Carnot cycle consists of the following steps, supposing the cycle to begin with the medium in the expanded state at the lower temperature.

1. Isentropic adiabatic compression to the higher temperature. This is represented by the line *ab* in the chart.

2. Isothermal compression, represented by the line *be* which is drawn to represent compression of the superheated vapor along *bc* until liquefaction begins, condensation of vapor along *cd*, and a slight compression of the liquid along *de*. During this compression the fluid gives off heat.

3. Adiabatic expansion to the lower temperature, represented by the line *ef*.

4. Isothermal expansion to the original condition, with absorption of heat at the lower temperature. This is represented by *fa*.

In this ideal cycle there must be no friction, no stray heat transfer and no expansion without work, as in a throttle; in brief, the cycle must be reversible.

The area *begh* extending to the absolute zero of temperature represents the heat energy delivered at the higher temperature, the area *afgh* represents the heat energy absorbed at the lower temperature, and the difference between the two, which is the area *abef* must therefore, because of the conservation of energy, represent the work done upon the system. The coefficient of performance is obtained by dividing the area *afgh* by the area *abef*. A similar relation of areas applies for any other reversible cycle.

THE REVERSED JOULE CYCLE.—Among the causes of departure from ideal conditions in practice is the impossibility of strictly isothermal expansion or compression of a dry gas or vapor. When the change is as rapid as it must be in practice, the time is not sufficient for the fluid to maintain a nearly constant temperature by transfer of heat to or from its surroundings.

The first part of the compression stroke of a compressor increases the pressure until it reaches that of the high pressure capacity, when the outlet valve opens. The pressure difference required to operate the valve may be considered negligible. In this first stage, which is represented by the line *ab*, the compression is nearly isentropic, and one step in a Carnot cycle has thus been realized approximately, but the next step involving isothermal compression with delivery of heat would require infinite time if the temperature of the working fluid were kept as low as that of the cooling agent. To effect the necessary delivery of heat the gas or vapor must be raised to a still higher temperature than that represented by the point *b* in Fig. 1, which we may consider to be the lowest temperature available before the operation of the system,

usually the temperature of the cooling water. The adiabatic compression must be continued until some higher temperature is reached, such as that represented by the point *b* in Fig. 2. The medium is then pushed out of the cylinder into a cooler where its temperature falls to that of the cooling water. The isothermal compression of the Carnot cycle is replaced by contraction at constant pressure, represented by the line *bcde* in Fig. 2. This contraction is isothermal only in the stage *cd*, in which the vapor is condensed at constant pressure.

For similar reasons when the fluid is in the form of gas or vapor the isothermal expansion at the lower temperature must be replaced by expansion at constant pressure. In Fig. 2 this expansion is represented, by the line *fa*, as occurring entirely in a mixture of liquid and vapor, which is a suitable condition for a carbon dioxide refrigerating system. The expansion is then isothermal as well as isopiestic. The isentropic step *ef*, like *ab*, can be realized approximately.

This cycle, consisting of two adiabatic stages and two stages at constant pressure is the same as that proposed by Joule for use in an engine operated by the expansion of heated air, save that in a refrigerating system the cycle is carried out in the reverse direction. It may be called a reversed Joule cycle.

Since the Joule cycle of the working fluid considered without regard to other parts of the apparatus, is reversible, its coefficient of performance can be estimated from the temperature-entropy chart in the same way as for the Carnot cycle. Thus the heat absorbed at the lower temperature is represented by the area under *fa*, the work done by the area of the cycle, and the coefficient of performance by the ratio of the two. This coefficient is less than that of the Carnot cycle but when, as in Fig. 2, the changes at constant pressure occur largely in a liquid-vapor mixture, and are therefore isothermal, the coefficient is not much less.

THE CYCLE WITH THROTTLE EXPANSION.—The practical application of the reversed Joule cycle requires both a compressor and an expansion engine. However, if the adiabatic expansion is replaced by expansion through a throttle, the other three stages can be carried out by a single cylinder, or a set of cylinders in a compound compressor. This involves a further loss of efficiency, but if the fluid is a suitable one the coefficient of performance can still be kept quite high.

It can be shown that when a fluid expands through a throttle there is no change in heat content, provided that any kinetic energy imparted to the fluid by expansion is so nearly dissipated into heat energy that the difference between the initial and the final kinetic energy is insig-

nificant and that the expansion is so rapid as to be sensibly adiabatic. Consequently such a change is represented on the temperature-entropy or the Mollier chart by a line of constant heat content. A cycle with throttle expansion is shown in Fig. 3, this expansion being represented by the line *ef*.

The amount of heat absorbed at the lower temperature corresponds to the area under the line *fa* which represents a reversible change; the amount of heat delivered at the higher temperatures corresponds to the area under the line *bcde*, which also represents a reversible change. The work done is proportional to the difference between these two areas, but not to the area of the cycle, as in the case of a wholly reversible cycle.

The coefficient of performance in the cycle in the diagram, which involves mainly changes in a liquid-vapor mixture, is not very much less than that of a Carnot cycle, but if the cycle were carried out entirely in a gas or vapor, as for example when air is used as a refrigerating medium, the coefficient of performance would be much less. This coefficient approaches more nearly that of a Carnot cycle of the same temperature range the farther the temperatures are below the critical point of the medium. This is an indication for the selection for a refrigerating system of a medium of high critical temperature, but this must not be carried too far, for if the critical temperature is high, the vapor pressure is low, the volume of the vapor is large and the equipment required is likely to be bulky and to have large friction losses. High heat of vaporization and low specific heat of the liquid are favorable to efficiency.

HEAT INTERCHANGE.—In case the temperature to be produced is quite low the efficiency of the cooling system may be reduced owing to the circumstance that only the cold obtainable from the refrigerant when its temperature is low is utilized, while the heat it takes in when warmed from this temperature to that of the compressor may represent a loss of refrigeration. In an ordinary refrigerating system, in which the medium is liquefied before expansion, this loss is negligible, because most of the heat absorption occurs in the process of evaporation and this process may even not be quite completed when the medium enters the compressor, and the introduction of the medium in a cold condition diminishes the work of compression. But when air or a similar gas is used and there is no liquefaction as part of the cycle, this loss may include the larger part of the refrigeration. Under such circumstances the cold contained in the gas leaving the low temperature chamber

should be saved, by using it to cool the compressed gas before expansion. This is done by means of a heat interchanger, which is used whenever a gas of low critical temperature is to be liquefied or when air is used as a medium for producing low temperatures above its liquefaction temperature. It may also be of value when ordinary refrigerants, such as carbon dioxide, are used to produce temperatures near the lower limits obtainable with such substances.

THE JOULE-THOMSON EFFECT AND THE THEORY OF THE HAMPSON LIQUEFIER.—The system employing throttle expansion with a heat interchanger may be used, as described, as a refrigerating system, the medium being preferably one that liquefies at the higher pressure employed. This system is identical in principle with the Hampson apparatus for the liquefaction of air and other gases, except that in the Hampson apparatus the liquid produced is removed from the system. The Hampson apparatus is the simplest form of an air liquefier and the one most often employed in laboratories.

The Joule-Thomson effect is the change of temperature produced in the expansion of a fluid through a throttle or porous plug when any increase of kinetic energy produced by the expansion has been dissipated into heat energy. We will consider first only the case in which this condition is satisfied. If in such a change there is no transfer of heat to or from the surroundings the heat content of the fluid must remain constant. In considering the effectiveness of the operation for the liquefaction of a gas it is convenient to consider not the rate of change of temperature with decrease of pressure, $-\left(\frac{\partial T}{\partial p}\right)_H$, but the rate of the heat absorption with decrease of pressure that would occur if instead of the heat content being maintained constant the temperature were maintained constant.

It can be shown that if C_p represents the specific heat at constant pressure this rate of heat absorption is $-C_p\left(\frac{\partial T}{\partial p}\right)_H$ and is equal to the rate of increase in heat content $-\left(\frac{\partial H}{\partial p}\right)_T$. This quantity is commonly represented by ρ. Since by definition $H = E + pv$,

$$\rho = -\left(\frac{\partial E}{\partial p}\right)_T - \left(\frac{\partial (pv)}{\partial p}\right)_T$$

This shows that the effect is made up of two parts. The first, corresponding to the change in internal energy, is the cooling produced as the

result of the molecules of the fluid moving away from each other against the restraining influence of molecular attraction, and thereby being retarded. This is the effect sought by Gay-Lussac and by Joule in their experiments on the expansion of a gas into an evacuated space. The second part of the effect depends upon the relation of pressure to volume. The work done upon a unit mass of the fluid in driving it through the throttle or porous plug is p_1v_1, where p_1 and v_1 are the initial pressure and volume; the work done by the unit mass in moving against the final pressure is p_2v_2, where p_2 and v_2 are the final pressure and volume. While for the ideal gas p_1v_1 and p_2v_2 are equal by definition, for real gases they are not equal, and hence a change of temperature results, corresponding to the heat energy added to or removed from the fluid as a consequence of this work. The effect due to molecular attraction is always a cooling; that due to the change in pv may be either heating or cooling. At sufficiently low temperatures the net Joule-Thomson effect is a cooling. At high temperatures the net effect may be a heating and there is then an intermediate inversion temperature at which the effect is zero. For most gases this inversion temperature is above ordinary temperatures, but for hydrogen it is about $-78.6°C$[11] for low pressures and somewhat lower at high pressures. Consequently in a hydrogen liquefier the gas must be precooled below this temperature; practically it must be precooled very far below it. At a temperature below the inversion point of the Joule-Thomson effect, the second term, which represents a heating at higher temperatures, passes through zero. When this term is equal to zero the Joule-Thomson cooling is represented by the first term. This temperature, which is called the Boyle point, is more easily determined than the Joule-Thomson inversion point. It is $-165.72°C$ for hydrogen[12] and about $-253°C$ for helium.[13]

The quantity ρ is connected by a thermodynamic relation with the expansion coefficient and the specific volume.[14] When these quantities are known the cooling produced can be calculated from them. The relation is

$$Q \equiv \int_{p_2}^{p_1} \rho dp = \int_{p_2}^{p_1} (T\alpha v_0 - v)dp$$

[11] Keesom, Leiden Communications. Supplement 39a.

[12] Kamerlingh Onnes and Brach, Leiden Communication No. 100a; 1907.

[13] Kamerlingh Onnes, Leiden Communication No. 102c; 1908.

[14] Buckingham, The Theory of the Hampson Liquefier, Bureau of Standards, Bull. 6, p. 125; 1909 (Reprint No. 123). The paper includes a chart of ρ for air at 16°C calculated from the data of Witkowski.

in which T is the absolute temperature, v_0 and v are the specific volumes at 0°C and at T, as functions of pressure, and α is the expansion coefficient, $\frac{1}{V_0}\left(\frac{\partial v}{\partial T}\right)$, at temperature T.[15]

The state of the gas entering the interchanger of a Hampson liquefier is entirely determined by its temperature T_1 and its pressure p_1, provided its kinetic energy is negligible. Similarly the state of gas leaving the interchanger with negligible kinetic energy is determined by its slightly lower temperature T_2 and its pressure p_2. Since in this apparatus no energy is taken from the gas as mechanical work, the heat it absorbs in its passage through the apparatus is entirely determined by these temperatures and pressures, and is independent of the internal construction of the apparatus, except as this affects the temperature of the outgoing gas. If the temperature of the outgoing gas were exactly that of the incoming gas the total absorption of heat would be equal to the value of Q for this temperature, regardless of the changes of temperature that may occur in the gas in its passage through the liquefier. The slightly lower value of the outlet temperature will not change the total Joule-Thomson heat absorption to a considerable extent, but to find the available heat absorption we must subtract from it the quantity $\int_{T_2}^{T_1} C_p dT$ which represents loss of refrigeration in the outgoing gas. In this, C_p represents the specific heat at constant pressure, which is in this case atmospheric pressure. Since the temperature range is small, C_p is practically constant and the loss of refrigeration is $C_p(T_1-T_2)$. For air at ordinary temperature C_p is nearly constant at about 0.24 over a wide range of pressure. For air at low temperatures, also, C_p is not very different from 0.24 provided the pressure is low, but for low temperatures combined with high pressures it varies widely.[16] There is a further loss of refrigeration as the result of the entrance of heat through the insulation. Let Q_1 represent the amount of this leakage per gram of air fed in. If W represents the work done on the system per gram of gas, the maximum coefficient of performance is

$$\frac{\int_{p_2}^{p_1} \rho dp - C_p(T_1-T_2) - Q_1}{W}$$

[15] A bibliography and a historical summary of experimental work on the Joule-Thomson effect are contained in a paper by Hoxton, Phys. Rev., *13*, p. 438, 1919. For recent work on air see Noell, Zeits. Vereines Deutsch. Ing., *62*, pp. 49 and 63; 1918; Keyes, Am. Chem. Soc., J. *43*, p. 1452; 1921; Roebuck, Phys. Rev., *19*, p. 406; 1922.

[16] A chart of C_p for air was published by Witkowski, Phil. Mag., (5) *42*, p. 1; 1896.

However, in laboratory practice the quantity W and the coefficient of performance are likely to be of less interest than the numerator of this coefficient, which represents the amount of heat absorption obtained per unit mass of gas.

The fraction of the gas that can be liquefied can be readily calculated when this numerator is known. If L is the latent heat of evaporation and T_B the boiling point, the cooling required to liquefy a unit mass is $L+C_p(T_1-T_B)$ and the fraction that can be liquefied is

$$\frac{\int_{p_2}^{p_1}\rho dp - C_p(T_1-T_2)-Q_1}{L+C_p(T_1-T_B)}$$

Since the Joule-Thomson cooling is not a large quantity the performance of the apparatus may be influenced greatly by relatively small changes in the temperature difference T_1-T_2.

PRECOOLING AND THE "CASCADE" SYSTEM.—There are several advantages and some disadvantages in precooling the compressed refrigerating fluid by a separate cooling system before it is permitted to expand. This procedure increases the amount of refrigeration at the lower temperature and therefore increases the amount of liquefaction. These gains result largely from the fact that the Joule-Thomson effect is increased by reducing the temperature. Also the quantity $C_p(T_1-T_B)$ is diminished by the reduction of the temperature T_1. Buckingham[17] has calculated on the basis of Witkowski's data for air with an initial pressure of 130 atmospheres, the upper limit of Witkowski's experiments, the following maximum yields of liquid:

Temperature Centigrade	Maximum Yield Per Cent
+16°	6.3
−35°	9.2
−78.5°	14.4

The working pressure used is likely to be higher than 130 atmospheres, but these data show the influence of precooling upon the yield. At 180 atmospheres, Bradley and Rowe[18] record the liquefaction of 8.8 per cent of the air with an initial temperature of 2°. In this case the output was about 1/2 liter of liquid per horsepower-hour. This is above the average for a Hampson liquefier with the stated degree of precooling.

[17] Loc. cit.

[18] Phys. Rev. *19*, p. 330, 1904.

For hydrogen with an initial pressure of 60 atmospheres Buckingham found by calculation:

Temperature Centigrade	Maximum Yield Per Cent
−190°	8.3
−212°	16.2

When the inversion temperature of the Joule-Thomson effect is below ordinary temperature, as in the case of hydrogen, it is of course absolutely necessary that the precooling be carried below the inversion temperature.

Not only does precooling increase the yield of the liquefier, but it may increase the coefficient of performance of the system as a whole, for while additional power is required to operate the precooling system, assuming it to be a mechanical system, the refrigeration obtained at the lowest temperature may be increased in greater proportion. This arises from the fact that refrigerating systems using ammonia or other media that are liquefied in the cycle are much more efficient than the air cycle. However, from the laboratory standpoint, a saving of power is usually of less importance than other considerations, such as the actual yield and the simplicity of the apparatus.

The precooling method may be amplified into the "cascade system," in which several refrigerating systems of different temperature ranges are employed, each being used to precool the fluid of the next lower temperature range. The cascade system was very important before the introduction of the heat interchanger as in the liquefiers of Hampson and Linde, but since that introduction its importance has diminished. It has the advantage of being capable of providing directly, for experimental purposes, liquid baths or cooling systems of several intermediate temperatures, although the same results can be obtained, with greater power consumption and perhaps less satisfactorily, by employing a substance at a very low temperature, such as liquid air, to produce intermediate temperature. Among the substances that have been used for producing temperatures between that of liquid air and those produced by commercial refrigerating systems are nitrous oxide (boiling point −89.5°), ethylene (−103.7°), methane (−161.4°) and oxygen (−183°).

The disadvantages of a precooling system and especially of the cascade system lie in the increase in equipment with consequent increase of first cost, upkeep and difficulty of operation.

THE LINDE SYSTEM.—In the Hampson liquefier, the lower pressure of the cycle is the pressure of the atmosphere. This is practically convenient, but what would be the influence on the performance of the system if the lower pressure were higher than atmospheric pressure? The Joule-Thomson effect does not vary greatly with pressure except at quite high pressures. Thus an increase of the outlet pressure from 1 atmosphere to 4 atmospheres, the high pressure being, say, 200 atmospheres, would produce only a small change in the Joule-Thomson effect, a change not very much more than the 3 parts in 200 that it would be if the effect were proportional to the pressure difference. The change in the amount of work done in compression would be considerable, however. To produce a pressure of 200 atmospheres a four-stage compressor might be used, increasing the pressure in the ratio of about 3.8 to 1 in each stage, and since the work done in compression is proportional approximately to the ratio of pressures, the work would be about equally divided among the four stages. Thus, the raising of the intake pressure from one atmosphere to four would permit the elimination of the first stage and reduce the work by about one-fourth.

This principle has been employed in the Linde[19] method of producing liquid air, and more especially, of separating air into its constituents. In this method the valve expansion reduces the pressure from about 200 to from 20 to 50 atmospheres. The liquid air is produced at this high pressure. If the pressure is reduced to atmospheric pressure, a considerable part of the liquid will boil away, the heat of evaporation being employed in cooling the remaining liquid to its normal boiling point, but this loss of liquid is less than the gain resulting from the use of the Linde principle, and the cold of the evaporated air can be employed in the interchanger in cooling the compressed air. The Linde interchanger differs from the Hampson interchanger because the main air streams between which heat is to be exchanged are both under pressure. The Linde interchanger is constructed by placing one or more small tubes inside of a larger one, thus forming two or more channels for the flow of air. Two compressors are employed. One compresses air to the low pressure of the cycle to replace the air removed from the cycle as liquid, or as separated oxygen and nitrogen, in case an equipment for effecting such a separation by fractional distillation is included. The other operates within the cycle. Both operations can be carried out in a single compressor of suitable design.

[19] U. S. Patents 727650, 728173, 815544.

THE CLAUDE SYSTEM.—It was pointed out that in ordinary refrigerating machines employing ammonia, carbon dioxide or some similar substance which is liquefied on the high pressure side of the system, the use of an expansion engine can be dispensed with without very great loss of efficiency, because the cooling produced by the evaporation of the liquid is greater than the additional cooling obtainable by causing the fluid to expend energy in an engine. On the other hand, when the fluid is air or some other gas that is not liquefied in the precooling before expansion, the cooling that would be produced by expansion in an engine may be an important addition to the small amount of cooling produced by the Joule-Thomson effect. In work on an industrial scale such engines have been employed. They are less often used in laboratory equipment.

When the expansion occurs entirely in an engine the cycle is the reversed Joule cycle. When the object is the production of liquid air, production of the lowest temperature in the engine would offer the practical difficulty of the operation of an engine containing liquid air, and, by making the lower temperature of the cycle very low, would give a lower coefficient of performance than in a cycle in which this temperature is higher. But to produce a liquid from a gas it is not necessary that the temperature should be lowered to the boiling point of the liquefied gas at one atmosphere pressure. It is necessary only to lower it sufficiently to produce liquid under pressure by either a continuous or a discontinuous change from the gaseous state. The pressure on the liquid so produced can then be reduced to one atmosphere, with partial evaporation. This principle is employed in Claude's system[20] for liquefying air, in which the expansion in an engine produces a temperature only a little below the critical temperature of $-140°C$. The expanded air, being at low pressure, does not liquefy, but is used to cool and liquefy air at high pressure.

In place of carrying out the expansion in one stage, Claude has also employed two stages with intermediate heat transfer. Increasing the number of stages increases the amount of work done by the expanding air and so increases the efficiency of the system, provided of course that the gain in work is not lost in increased friction. This is analogous to the decrease of the work that must be done in the adiabatic compression of a gas if the compression is carried out in several stages with intermediate cooling.

[20] Claude, Liquid Air Oxygen Nitrogen, English translation by Cottrell (1913); U. S. Patents 967104, 1027817.

Norton[21] has introduced an improvement over the Claude system by carrying out the expansion at more than one stage of the cooling, with an increase in thermodynamic efficiency. Such a system, with its multiplication of machines, is obviously adapted rather to industrial work than to laboratory purposes.

OTHER METHODS OF REMOVING ENERGY FROM EXPANDING GAS.—The use of a piston engine or turbine engine for cooling gas by the performance of work, while feasible on a large scale, is not adapted to small apparatus. However, some other methods of removing energy from the gas have been tried recently.

The theory of the Joule-Thomson effect that has been presented related to the case in which any change in kinetic energy produced by the expansion is negligible, which requires that either no great change in velocity shall be produced or that if a high velocity is produced its kinetic energy shall be dissipated as heat before the gas leaves the interchanger. On the other hand, if the gas could be caused to leave the interchanger at a very high velocity a corresponding amount of heat energy would have been removed from the gas and converted into mechanical energy and retained in this condition until the cold so produced could be utilized, in part at least. The possibilities of this method are being investigated by Davis and Kleinschmidt,[22] who have been able in preliminary experiments to increase the temperature of the outgoing gas, measured after the gas had emerged and the kinetic energy had been dissipated, to 4° *above* the temperature of the entering gas. The temperature of the gas while emerging at high velocity was probably slightly less than that of the ingoing gas.

Meissner[23] has proposed to charge electrically the gas issuing from the expansion nozzle and cause it to carry the charge in a direction opposed to a restraining electric force, thereby diminishing the velocity and preventing part of the kinetic energy from being converted into heat.

REFRIGERATION BY THE ABSORPTION SYSTEM.—The absorption system is not strictly a mechanical system, but produces cold by the application of heat without the intermediation of mechanical energy. It depends upon the use of a substance the vapor of which is strongly absorbed by some other material. The working fluid most often used is

[21] U. S. Patents, 1264845 and 1292958.
[22] Private communication.
[23] Deutsch. Phys. Gesell., Verh., *21*, p. 369; 1919.

ammonia, its vapor being absorbed by water or a salt. Water itself has also been used as a working fluid, its vapor being absorbed by sulphuric acid. The operation consists of two principal steps. In the first the working fluid, ammonia for example, is permitted to evaporate while its vapor passes to the absorbing material, water for example, which is kept as cool as feasible. The ammonia is thus cooled to a low temperature by its own evaporation. In the second step the ammonia is recovered from the water solution by heating the water, the ammonia vapor being condensed by cooling, usually by circulating water.

This system has no coefficient of performance in the sense in which the term has been defined, since it does not employ mechanical work. The important characteristic is the ratio of the heat absorbed at the low temperature to that applied at the high temperature.

In an ordinary ammonia absorption system in which the ammonia is absorbed in water, this heat ratio is in the neighborhood of 1/4. In spite of the incomplete conversion of heat energy into mechanical work in the motive engine of the ammonia compression system, the absorption system is less efficient than the compression system, except in the production of very low temperatures. In the Seay system, in which the ammonia is absorbed in solid ammonium salts, the efficiency is higher than in the water absorption system.

When water is the refrigerating fluid a vacuum must be maintained in the system, because the vapor pressure of water at low temperatures is so low. While the system might be made to operate in the presence of air, the air would so impede the passage of water vapor from the low temperature evaporator to the absorber that the action would be extremely slow. It is therefore necessary to employ a vacuum pump to remove the air and perhaps also to continue to operate it occasionally or continually to remove air evolved from the water or admitted by leaks. The water may be frozen while boiling under the reduced pressure. If brine is used instead of water, temperatures below 0° can be reached.

The absorption system is now less used industrially than the compression system, mainly for reasons of efficiency. It has, however, some advantages, which may recommend it for special purposes. It does not require moving machinery as an essential part, though the water vapor system requires a vacuum pump as stated, and in ammonia systems of large size a pump is employed to produce circulation. It is possible to obtain quite large refrigerating capacity in an ammonia absorption system of small proportions, and large fluctuations in the

rate at which refrigeration is employed produce less disturbance in the system than in a compression system.

REFRIGERATING FLUIDS.—The choice of a fluid for refrigeration by the compression system will depend upon the temperature desired, the size of the installation, the thermodynamic properties of the fluids, the operating pressures they require, and upon their corrosiveness, their

TABLE 3.

Material	Critical Tempera- centigrade	Boiling Point	Freezing Point	Heat of Vaporization at Boiling Point calories per gram	Other Properties
Ammonia	132.4°	−33.4°	−77°	327	Harmful except in small quantities; corrodes copper and brass if not dry; not readily combustible.
Sulphur dioxide	157.2°	−10.0°	−73°	91(0°)	Harmful; corrodes copper and brass if not dry.
Carbon dioxide	31.1°	−78.5° (sublim- ation)	−57°	86(−57°) (liquid)	Nearly harmless, not corro- sive.
Methyl chloride	143.1°	−24.1°	−103.6°	97(0°)	Anaesthetic, inflammable, not corrosive.
Ethyl chloride	183.°	+14°	−142°	83	Anaesthetic, inflammable, not corrosive.
Nitrous oxide	36.5°	−89.5°	−102.4°	67(−20°)	Anaesthetic, not inflammable, not corrosive.
Methane	−82.8°	−161.4°	−183.15°	122	Nearly harmless, inflammable, not corrosive.
Ethane	32.1°	−93°	−171°		Nearly harmless, inflammable not corrosive.
Propane	95.6°	−37°	−195°		Nearly harmless, inflammable not corrosive.
Ethylene	9.5°	−103.7°	−169°		Anaesthetic, inflammable, not corrosive.
Air	−140.7°	−194°	−209.86° to −218.4°	51	

harmfulness when inhaled, their inflammability and their cost. Some of the properties of the more important substances are given in Table 3.

Industrially, ammonia is most used in large installations, and gives in general greater actual coefficient of performance than other refrigerants; sulphur dioxide is adapted to very small units, as in household refrigerators, because of the low pressures required, though ammonia is also used in small units, while carbon dioxide is especially suitable for use on shipboard or in other confined spaces where the accidental release of large quantities of ammonia or especially sulphur dioxide would be very dangerous to life.

From the laboratory standpoint carbon dioxide has an advantage over ammonia and sulphur dioxide in being capable of producing somewhat lower temperatures. Temperatures down to the freezing point of carbon dioxide ($-57°$) can be produced. Ethylene is capable of producing considerably lower temperatures, and fills a place intermediate between the industrial refrigerants and liquid air or liquid oxygen.

REFRIGERATING PLANTS.—No attempt will be made here to give details of the construction of refrigerating plants, because the subject is a large one, relating rather to industrial practice than to laboratory practice, and because refrigerating apparatus adapted to the ordinary temperature ranges can readily be purchased in various forms.

About the smallest mechanical refrigerating systems in use are those now being quite extensively introduced for use in household refrigerators. The mechanism of such refrigerators can sometimes be purchased separately and should be of use for some laboratory purposes.

A refrigerating system of the compression type comprises in general a compressor, an oil trap, a condenser, a liquid tank, an expansion valve and a refrigerating coil.

When especially low temperatures are required it may be desirable to use an interchanger. If the fluid is carbon dioxide or if it is air with the return line under pressure the interchanger may consist of two lengths of copper tubing either placed one inside of the other or soldered together side by side. The tubes may be coiled into a helix to reduce the space required, and covered with insulation.

When refrigeration is required in large spaces or at a distance from the compressor, either the refrigerating fluid may be piped to the required place and refrigeration produced by expansion, or a brine containing calcium chloride or sodium chloride may be cooled by the refrigerating fluid and circulated to the required points. The use of

brine may diminish the leakage of the refrigerant, with its attendant waste, and diminish the danger of the accidental release of a harmful or inflammable vapor.

CONSTRUCTION OF THE HAMPSON LIQUEFIER.—A diagram of a form of Hampson liquefier is presented in Fig. 4. It comprises a heat interchanger consisting of a long coil of copper tubing *aa'* through which

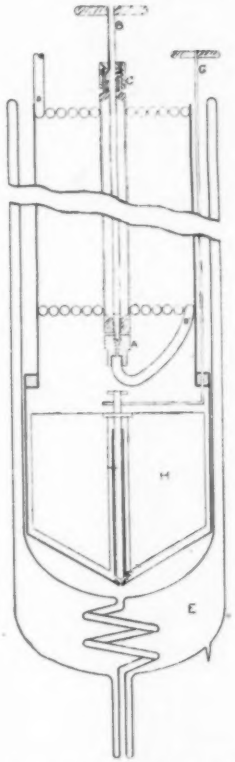

FIG. 4. *A form of Hampson liquefier.*

the compressed air passes, an expansion valve *A* operated by a stem *B*, an insulating container consisting, in this design, of a vacuum vessel *E* with an outlet at the bottom, and a float-valve *F* designed to permit the exit of only liquid at the bottom.

The copper coil consists of a single length of tubing wound in a series of flat spirals one above another, with the air current in the first spiral

passing from the outside to the inside, in the second from the inside to the outside and so on. This shape may be given to the coil by winding the tubing upon suitable forms, which are illustrated in a paper by Cook,[24] which contains other details relative to liquefiers. Joints are best made with silver solder. The use of two or more tubes wound in parallel does not produce as good heat exchange as a single tube of the same diameter;[25] it has the advantage, however, of reducing the pressure drop. Bichowsky[26] has recently described a liquefier constructed by Nelson in which the interchanger consists of a copper tube rolled flat and then twisted to prevent it from being expanded by the pressure. The heat exchange in this tube was so good that a liquefier producing 3.5 liters of liquid air per hour required only 2 meters of tube.

In winding coils of copper tubing for liquefiers, and often for other laboratory purposes, it may be necessary to employ some means of preventing the tube from becoming flattened in bending. One method of preventing this consists of filling the tube with water and maintaining it at high pressure by means of a hand-operated hydraulic pump. The pressure required will depend of course upon the size of the tubing; for a Hampson liquefier about 200 atmospheres will usually be suitable. Since the bending of the tube under pressure may increase its capacity the pump must be operated continually during the bending, to maintain the pressure.

Another method, due to Stimson, consists of filling the tube with water, after annealing it, and freezing the water by surrounding the tube with ice and salt, and bending the tube while cold. If a very sharp bend is to be made the tube may be bent only part way at first, then emptied and annealed and the process repeated with further bending.

The interchanger coil is mounted in a close-fitting tube, made of thin metal. German silver is a suitable metal, because it has a low thermal conductivity and does not rust. The valve stem *B* and its surrounding tube are made rather light, to diminish heat conduction. The stuffing box *C* has to hold only the small back pressure.

The outlet valve *F* is controlled by a float *H*, which opens the valve only when there is a sufficient quantity of liquid air in the vessel. This

[24] The Production of Liquid Air on a Laboratory Scale, Bureau of Standards Scientific Paper No. 419, (1921). Fig. 4, was taken from this paper.

[25] Travers, Gwyer and Usher, Smithsonian Miscellaneous Collections. No. 1652; 1906.

[26] Jour. Ind. Eng. Chem., *14*, p. 62; 1922.

prevents unliquefied air from leaving the container without passing over the heat interchanger. The rod *G* makes it possible to hold the float valve open. This may be done when it is desired to dry the apparatus by a current of air before it is put in operation, in order to prevent the float valve from becoming stuck by freezing. The automatic operation of such a float valve may be interfered with by the violent motion of the air coming from the expansion valve. To prevent this it has been found sufficient to fasten several layers of fine wire gauze around the expansion valve. The float valve may be replaced by a valve operated by hand by means of a long stem. This requires considerable attention during operation. The valve may also be dispensed with entirely, but with a loss in efficiency, unless the outlet is very small, in which case it may become clogged.

In any but the very smallest liquefiers the vacuum vessel *E* can be replaced by an ordinary insulating material, such as "regranulated" cork, with some loss of efficiency. Very small liquefiers are sometimes surrounded by a vacuum vessel having no outlet at the bottom, the vessel being withdrawn from around the interchanger when a few hundred cubic centimeters of liquid have been obtained.

To give an idea of suitable dimensions, those of a liquefier at the Bureau of Standards will be stated. This liquefier is of such size that about one cubic meter per minute of free air can be driven through it by a pressure of 180 atmospheres. The copper tubing is of 4.8 cm (3/16 inch) outside diameter and 0.89 mm wall. Its total length is about 60 meters. The coil is about 46 cm long and 7.6 cm in diameter. This liquefier produces approximately eight liters of liquid air per hour when the air is pre-cooled by brine from a refrigerating plant.

Air liquefiers can be purchased ready made, including one form of such small size that it can be operated by means of one or two cylinders of compressed air, with the production of a few hundred cubic centimenters of liquid.[27]

PURIFYING THE AIR.—It is necessary to remove the greater part of the water and carbon dioxide of the air before it enters the liquefier;

[27] Following are some additional papers relative to the Hampson liquefier, including, more especially, the comparatively recent ones:

Travers, Smithsonian Misc. Coll. No. 1441, 1904; Study of Gases, pp. 190-195; 1901.
Allen and Ambler, Phys. Rev., *15*, p. 184; 1902.
Bradley and Rowe, Phys. Rev., *19*. p. 330, 1904.
Bradley and Hale, Phys. Rev., *19*. p. 387; 1904.
Hudson and Garland, Univ. of Ill. Eng. Exp. Sta. Bul. No. 21, 1908.
Kamerlingh Onnes, Leiden Comm. 94f; 1906.

otherwise these materials would clog the liquefier by freezing in it. Complete purification is not necessary, however, because small amounts of ice or solid carbon dioxide are driven through without clogging when the liquefier is operated only a few hours at a time. Liquid air so obtained is turbid from the presence of this material. This does not matter for most purposes, and the liquid can easily be rendered clear by filtering through filter paper. The amount of turbidity gives an indication of the condition of the purifiers.

The air may be purified either before or after compression. The former method has the advantage that the purifying equipment is not required to stand high pressure, but there is danger that the purifying material may be drawn into the compressor and interfere with valves. Purifying after compression has the advantage that the apparatus can be made much smaller without an excessive velocity of flow, and also with this arrangement a large part of the water in the air is condensed out in the water coolers after compression and collects in the oil trap, where it can be drained out, thus diminishing the amount of water that must be removed by the dryer.

Suitable purifying materials are sodium hydroxide solution for removing carbon dioxide and anhydrous calcium chloride for removing water.

The purifier for removing carbon dioxide may consist of a long vertical steel tube filled with lumps of marble about half covered with the sodium hydroxide solution, the air entering at the bottom. The marble not only increases the surface but diminishes the carrying of spray. The purifier used with the liquefier mentioned is about 2.5 m long, and 11 cm in inside diameter and is charged with four liters of a 25 per cent solution of sodium hydroxide.

The calcium chloride purifier used with the same equipment comprises three separate vertical steel tubes each one meter long and 5 cm in inside diameter. Only one tube is refilled at one time, and this tube is then connected third in the series, thus economizing material. The air enters each tube at the bottom and each has a drain at the bottom for drawing off calcium chloride solution.

It is well to be sure that the calcium chloride used is really anhydrous or nearly so. The material sold in the United States as "anhydrous" is usually $CaCl_2 2H_2O$. The "calcined" material is supposed to have had the water of the "anhydrous" substance driven out, but frequently this is only half accomplished. When large quantities are purchased the maximum permissible water content should be specified.

In place of the materials mentioned, calcium hydroxide in water (milk of lime) can be used to remove carbon dioxide, or both water and carbon dioxide can be removed by solid sodium hydroxide or potassium hydroxide.

If the pure air exhausted from the liquefier is returned to the intake of the compressor this greatly diminishes the consumption of purifying material. The additional air required at the intake should be supplied through a pipe of such length and size that the pure air can not surge out through it. With this arrangement it has been found unnecessary to employ any purifier to remove carbon dioxide when the liquefier is operated only a few hours at a time.

OPERATION OF THE HAMPSON LIQUEFIER.—When the equipment is put in operation there is less chance of clogging with ice if the expansion valve is open when the compressor is started, so that the rate of flow gradually increases as the pressure rises, instead of the valve being opened only when full pressure is reached. Clogging occurs most often at the valve and then can usually be relieved by manipulating the valve. The pressure gage should be watched for indications of clogging. If the liquefier becomes completely clogged by ice or carbon dioxide the remedy is to stop operation, allow the liquefier to warm, and dry it by circulating dry air through it, replenishing the purifiers, if necessary. Liquefiers sometimes become clogged with solid material. This may require the dismantling of the apparatus for repairs. This course has been avoided by pouring concentrated hydrochloric acid into the inlet of the liquefier, and following it by water under high pressure from a hydraulic pump. This acid does not act upon copper in the absence of air, but dissolves copper oxide scale and iron rust which are likely causes of clogging. It must not be allowed in contact with steel parts more than momentarily and should be washed out well after the obstruction is removed. The apparatus should then be dried by an air current. Oil spray from the compressor or the spray of solution from the carbon dioxide purifier are possible causes of clogging in the liquefier.

When the air begins to liquefy its rate of flow through the expansion valve increases and there is consequently a slight drop in the pressure.

THE LIQUEFACTION OF HYDROGEN.—The Hampson liquefier, is adapted to the liquefaction of air and some other gases in the form in which it has been described. Liquefiers of the Hampson type are used for the liquefaction of hydrogen, but since the inversion temperature of the Joule-Thomson effect for hydrogen is about $-80°C$ it is necessary to precool the compressed hydrogen below this temperature

before expansion. While cooling it a little below this temperature might be sufficient to liquefy a small fraction of the gas in a liquefier of nearly the maximum theoretical efficiency, it is practically necessary to carry the precooling to a much lower temperature, because the Joule-Thomson effect is very small at temperatures only a little below the inversion temperature. Even the temperature of liquid air at atmospheric pressure is hardly low enough, and the cooling is best carried to about $-205°$ by evaporating the liquid air at reduced pressure with the aid of a vacuum pump.

In the simplest design the liquid air required for precooling is produced by a separate liquefier and poured into the hydrogen precooler as required. Olszewski[28] constructed a hydrogen liquefier with an air liquefier incorporated in it.

The container of liquid air at reduced pressure, or any other apparatus maintained at a temperature below that of liquid air at atmospheric pressure, must be protected from contact with the atmosphere on its exterior, else the air would liquefy on its surface and thereby convey a large amount of heat to it. Such a vessel is best protected by a vacuum-walled container, though an insulating material with its pores filled with hydrogen can be used.

In the construction of a hydrogen liquefier, as in the construction of many other forms of thermal apparatus the operation of which may not be free from difficulties, it may be desirable to attach to important parts of the apparatus thermocouples made of fine wire, to permit the observation of temperatures during operation.

The difficulty most often encountered in the liquefaction of hydrogen has resulted from the presence of impurities in the hydrogen, which are frozen in the liquefier and tend to clog it. If the hydrogen is of an ordinary degree of purity the expansion valve is likely to become clogged before any liquid hydrogen has been collected. With somewhat better hydrogen it may be possible to obtain a quantity of liquid sufficient for many experimental purposes. Experiments requiring only small quantities have been made with the experimental apparatus placed directly in the same vacuum vessel in which liquid hydrogen is collected, which vessel may also provide the insulation for the hydrogen interchanger. This method avoids the loss involved in transferring the liquid.

[28] Bull. Intern. Acad. Sci. Cracovie, A. p. 1; 1912.

When the amount of impurity in the hydrogen is such that the liquefier can be operated only a few minutes without clogging, operation can be resumed after clogging by shutting off the hydrogen supply, warming the valve until the obstruction is melted out, and discarding the impure gas produced from it. The warming of the valve can be readily accomplished by passing a small quantity of pure dry hydrogen at room temperature into an opening at the bottom of the liquefier and causing the hydrogen to pass up around the expansion valve.[29] The valve might also be warmed by an electric heater, though this might involve danger of the ignition of an explosive mixture of frozen oxygen and liquid hydrogen and should therefore not be used. The operation of melting out the obstruction and renewing liquefication can usually be carried out very quickly.

If any considerable quantity of liquid hydrogen is required it is much better to employ very pure hydrogen. This may be obtained by the purification of commercial hydrogen or by the generation in the laboratory of hydrogen initially free from the more difficultly removable impurity.

The impurities most likely to produce clogging of the valve are nitrogen and oxygen. Small quantities of more readily condensible impurities, including water, carbon dioxide and the vapor of lubricating oil, are not likely to cause trouble, for they are condensed over a relatively large area in the interchanger where the hydrogen is first cooled, and not in the valve. Drying the hydrogen with calcium chloride reduces the water content sufficiently, at least for the production of several liters of liquid. Oxygen can be removed by passing the gas through heated platinized asbestos or heated palladiumized asbestos, or by heating the gas to a sufficiently high temperature without a catalytic agent. Nitrogen is the most difficult impurity to remove. Kamerlingh Onnes employs for the regular production of liquid hydrogen a purifier in which impurities are frozen out of the gaseous hydrogen by cooling it with liquid hydrogen. By means of an electrolytic generator, hydrogen can be produced in the laboratory containing so little nitrogen that if care is taken to avoid the introduction of air during the collecting and compression of the gas no purification to remove nitrogen is necessary.[30]

When hydrogen is collected in a gas holder containing water the entrance of air by diffusion through the water may be sufficient to cause

[29] Lilienfeld, Zeit. f. kompr. u. flüss. Gase, *13*, p. 189; 1911.

[30] A paper on the production of pure hydrogen for liquefaction is about to be published by the Bureau of Standards.

trouble. Air can also enter if mineral oil is used in place of water, though oil has an advantage in another way. In the process of liquefaction the hydrogen passes in circuit through the gas holder, the compressor, the drier and the liquefier, and the gas not liquefied returns to the holder. If water were used in the holder the gas would take up water at every circuit, thus imposing an unnecessary duty upon the drier. The use of oil avoids this. The solubility of most gases in glycerine is remarkably low. For this reason crude glycerine can be employed in a gas holder and the entrance of air is then very slight, even when the gas remained in the holder for a long time. Holders in which a liquid other than water is to be used should be constructed with an inner stationary bell, leaving only a narrow annular space for liquid. Otherwise the cost of glycerine or oil might be prohibitive. This type of construction itself diminishes the diffusion of air.

For details relative to the construction of hydrogen liquefiers the original papers[31] should be consulted.

LIQUEFACTION OF OTHER GASES.—The liquefaction of helium is accomplished by the use of a liquefier of the Hampson type with precooling by liquid hydrogen evaporated under reduced pressure until its temperature reaches the freezing point, $-259°$. The original papers[32] should be consulted for details.

Neon can be liquefied and frozen by cooling with liquid hydrogen. Many other gases can be liquefied easily by cooling with liquid air. Nearly pure liquid oxygen can be obtained from liquid air by means of a rectifying column or merely by the evaporation of the liquid. If pure gaseous oxygen at atmospheric pressure is to be liquefied, this is easily accomplished by passing it into a vessel immersed in freshly prepared

[31] Dewar, Roy. Soc. Proc., *63*, p. 256; 1898.
Description of British Exhibit at St. Louis, Engineer, *99*, pp. 540, 566, 590; 1905.
Travers, Phil. Mag. (6), *1*. p. 411; 1901; Study of Gases, p. 195; Smithsonian Misc. Coll. No. 1441; 1904.
Travers, Gwyer and Usher, Smithsonian Misc. Coll. No. 1652; 1906.
Kamerlingh Onnes, Leiden Communications, Nos. 94e, 94f; 1096.
Crommelin, Leiden Communications, Supplement No. 45.
Olszewski, Bull. Intern. Acad. Sci. Cracovie, A. p. 619; 1902; p. 241; 1903; p. 1; 1912.
Lilienfeld, Zeits. f. kompr. u. flüss. Gase, *13*, p. 186; 1911.
Nernst, Zeits. Elecktrochem. *17*, p. 735; 1911.
McLennan, Rov. Soc. Canada, Trans., *15*, Sect. *3*, p. 31; 1921.
McLennan and Shrum, Rov. Soc. Canada, Trans., *16*, Sec. 3, p. 181; 1922.
Bichowsky, Jour. Ind. Eng. Chem., *14*, p. 62; 1922.

[32] Kamerlingh Onnes, Leiden communications Nos. 108, 158, and Supplements No. 21a.
Crommelin, Leiden Communications Supplement No. 45.
McLennan and Shrum, Roy. Soc. Canada Trans. *16*, Sect. 3, p. 181; 1922.

liquid air. The oxygen should be dry, otherwise the ice formed on the walls of the vessel will greatly retard heat transfer. Liquid nitrogen can be obtained by means of a Hampson liquefier, or by passing dry nitrogen under pressure through a copper coil cooled with liquid air and releasing the liquid nitrogen through a slightly opened valve.

GAS COMPRESSORS.—Since compressors suitable for any gas or refrigerating medium likely to be employed in the laboratory can be purchased ready made, no detailed description of them is required, but some suggestions may be made as to their operation.

The compressors producing the highest pressures, such as those employed in the production of liquid air or liquid hydrogen, are those most likely to give difficulty. Such compressors may have as many as four or five cylinders, with means for cooling the gas by circulating water after each stage of compression, and after each stage a pressure gage and a safety valve are connected. It is very useful to have a simple flow meter of the orifice type in the gas stream, to give an indication of the behavior of the compressor, provided such a meter can be so connected as not to be disturbed by the pulsations of pressure. If the compressor is used in liquefying air or other gas the meter can be placed in the low-pressure exhaust of the liquefier. A correction can be made approximately for the gas that is liquefied and hence does not go through the meter. A meter can be easily constructed by placing an orifice within a length of rather large pipe and connecting a water manometer to indicate the pressure drop at the orifice.

The most common difficulty is the failure of the compressor to deliver a proper volume of gas. The trouble may originate in valve leakage, piston ring leakage, or leakage to the outside at a stuffing box, cylinder head gasket, defective safety valve or elsewhere. Leakage to the outside is usually easy to locate. If there is leakage at valves or piston rings, direct examination of the valves or rings may not reveal that they are leaky, but the pressure gages usually indicate the location of the trouble. The pressures the gages should indicate can be calculated approximately from the cylinder diameters. If either the inlet valve or the outlet valve of a cylinder leaks the gage on the high pressure side on the cylinder will indicate too low a pressure while the one on the low pressure side will indicate too much pressure. If the piston rings of a cylinder leak, the gage on the high pressure side will indicate too low a pressure, but the corresponding high pressure will not necessarily be on the next gage below. If, as is usually the case, compression is produced in only one end of the cylinder, the effect of piston leakage

depends upon what part of the system the space on the inoperative side of the piston head is vented to. If it is vented to the intake of the compressor, none of the gages will read high. If it is vented to the cooler between two stages the gage at this point will read high. Further guidance in the location of trouble can be obtained by observing how the gage readings change immediately after the compressor is stopped. These changes depend rather more upon piston leakage than upon valve leakage, and by comparing indications during operation and after stopping the two kinds of leakage can usually be more or less distinguished.

Leaky valves should be carefully re-ground. The grinding compounds sold for use on automobile engine valves may be used. If the piston head leaks it may be the result of worn rings, broken rings or a scored or worn cylinder. When a new compressor is first started there may be excessive piston friction and leakage. The compressor should be operated at low speed until the rings and the cylinders have been worn smooth. If a cylinder has become deeply scored or badly worn from long use it must be relined, or rebored. If it is rebored new piston rings of larger size will usually be required. A small cylinder that is only slightly worn can be put in good condition by lapping by hand.

The failure of an inner part of a cylinder head gasket may permit gas to be short-circuited past a valve, without leakage to the exterior.

Leaks causing small losses of gas to the atmosphere may not be important, but if a leak occurs at the first cylinder or in the intake pipe leading to it air may be sucked in through the leak as the result of a partial vacuum produced on the intake stroke. If a gas other than air is being compressed this causes contamination of the gas. Such contamination is most likely to occur at the stuffing box of the first cylinder. It can be avoided by constructing a second stuffing box outside the first one and piping the space between the two to the part of the compressor containing gas that has undergone the first compression. Some compressors are built with such an arrangement to diminish loss of gas by supplying to the space between the stuffiing boxes gas at lower pressure than that in the cylinder.

A compressor should be equipped with an oil trap to remove oil spray and condensed moisture.

The proper lubricant for a compressor depends upon the gas to be compressed. In high-pressure air compressors ordinary machine oil must not be used, since severe explosions may be produced by the ignition, as the result of the heat produced by compression, of a mixture of

oil vapor and compressed air. Oil for high pressure air compressors should have a flash point not lower than 200°C.

In the cylinders of oxygen compressors there must be no oil whatever; in fact any equipment containing compressed oxygen must be free from oil. Such compressors are lubricated with soap and water, or merely with water.

Sulphur dioxide acts upon many kinds of mineral oil, causing the separation of solid compounds. Oil should be used which has been treated with sulphur dioxide at the refinery with the removal of the solid material so produced.

Ammonia has little effect upon mineral oil, except that in the presence of moisture it sometimes emulsifies the oil and forms a sludge.

Some refrigerating media, including ethyl chloride, methyl chloride, methyl ether and ethyl ether are very soluble in mineral oil. Glycerine is the lubricating material most commonly used with such media.

Ordinary mineral lubricating oil is used with carbon dioxide.

Compressors and vacuum pumps of the rotary type and the jet type are sometimes employed when the pressure required is not high.

INSULATION.—For the best thermal insulation a vacuum-walled vessel is required. Heat is transmitted into such a vessel by conduction through the residual gas, by radiation, by conduction along the inner wall of the neck or of any other opening, and also in some cases through the gas within the neck or through apparatus inserted in the neck.

The conduction through the residual gas of the vacuum space can be rendered quite negligible by producing a sufficiently good vacuum. While the vessel is connected to the vacuum pump it should be heated for some time to drive out air or moisture from the surface of the walls.

The transmission of heat by radiation between the walls of a glass vessel can be reduced to a small fraction of its original magnitude by silvering the surfaces of the glass next to the vacuum space. Unsilvered glass vessels are sometimes of use however, because it is possible to see through the sides. This advantage can be retained in a silvered vessel to a limited extent by leaving a vertical strip on each side of the vessel unsilvered. This can be accomplished by laying the vessel in a horizontal position, running in silvering solution through a suitable tube until the vacuum space is somewhat less than half full, and, after this solution has deposited its silver, washing the vessel, placing it again in a horizontal position but with the other side up, and repeating the operation, leaving two narrow opposite strips unsilvered.

If a vessel has been silvered and well evacuated a large part of the residual heat transfer may be the conduction down the inner wall o the neck. For the best insulation the neck should therefore be as long, narrow and thin as circumstances permit. If the vessel is made of metal the neck must be extremely long and slender if the insulation is to be comparable with that obtainable in a glass vessel. When liquid air is placed in a vessel the rising column of evaporated air is denser than the atmosphere by reason of its low temperature and there is no convection and practically no heat reaches the interior through the ascending vapor. In the case of liquid hydrogen, however, the evaporated gas is lighter than the atmosphere in spite of its low temperature, and it is best to insert a plug of cotton in the neck of the vessel to prevent convection.

If liquid air is poured from the mouth of a glass vacuum vessel the vessel may be cracked by the unequal cooling of the joint at the mouth. This is not very likely to happen if the mouth is small and the joint is well made, especially if the vessel is rotated during pouring in order to cool all sides of the mouth about equally. Liquid air can be removed from a vessel without this risk by inserting a rubber stopper in the neck carrying a bent glass tube extending to the bottom of the vessel, and applying a little air pressure above the liquid, for example by a rubber atomizer bulb. A vacuum-walled tube may be employed.

If a vacuum vessel is made with an outlet at the bottom, provision must be made for the unequal contraction of the inner and the outer walls of the vessel when cold material is placed in it. This may be accomplished by means of a short helix in the outlet tube, as shown in Fig. 4.

There is an advantage in the use of pyrex glass in the construction of vacuum vessels, since by its use the danger of cracking as the result of temperature changes is practically eliminated in most cases.

When the best insulation is not required ordinary insulating materials such as cork, cotton, wool, hair felt, calorox, asbestos fiber and diatomaceous earth may be used. The thermal conductivities of these materials at ordinary temperatures range from .000076 to .000106 calories per second per square centimeter per centigrade degree per centimeter thickness.[23] If the insulating material around a cold object is exposed to the atmosphere it collects moisture, which diminishes the

[23] Van Dusen, Amer. Soc. Refrig. Eng. Jour. Nov. 1920, gives a table of the conductivities of these and many other materials. Copies of this table can be obtained from the Bureau of Standards.

insulation and causes some materials, calorox for example, to shrink together. This can be avoided by placing the material in an air-tight container to which only dry air is admitted, but this is not always convenient. If the insulation is to be exposed to moisture ground cork or cork board is about the most suitable material.

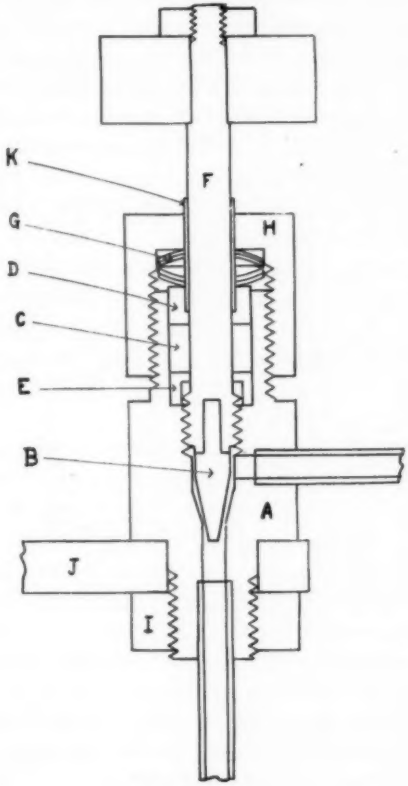

FIG. 5. *Valve.*

VALVES.—Fig. 5 shows a high pressure needle valve employed by Osborne, Stimson and Sligh of the Bureau of Standards, for calorimetric work, in which it was necessary that both the valve and its packing should remain perfectly tight for long periods when employed with either a high pressure or a vacuum. The valves made for this purpose were small, the length over all being about 6 centimeters and the diameter of the stems about 3 millimeters. For the control of larger

quantities of material, as in an air line leading to a liquefier, a similar valve of larger size is suitable, and when absolute tightness is not required the refinements of finish that will be described are not all necessary.

The valve body *A* is made of brass. Brass could not be used, however, with moist ammonia or sulphur dioxide, though it can be used with perfectly dry ammonia. For the calorimetric work the conical point or "needle" *B* was made of stainless steel, to avoid rusting in the presence of moisture. Since stainless steel is not easily threaded, the stem was more conveniently made of some other metal that will not rust, such as monel metal. For less severe requirements ordinary steel can be used, the point being preferably hardened. The thread on the stem was lapped smooth to reduce abrasion and friction, especially when the valve is under pressure. This, with the use of suitable packing, insures that most of the torque applied to the stem shall be used in seating the valve, and makes it easy to determine by the feeling when the valve is properly closed. The point and the seat should be nicely finished and should be accurately coaxial with the thread. An angle of 22° for the point and 28° for the conical seat were found suitable, though some other angles might be equally so.

The packing should be compressed under a pressure sufficient to make it yield like a fluid and greater than the pressure of the gas. Such a pressure can be produced by merely compressing the packing with a nut, but a slight yielding of the material can then release the pressure and permit a leak. To maintain the pressure on the packing, the cupped steel spring washers *G* were placed under the nut *H*. The loose sleeve *K* attached to the washer *D* is intended to prevent the scratching of the stem by these springs. Leather soaked in melted paraffin was used as packing material (*C*). This is compressed by the brass washers *D* and *E* which should be made to fit closely over part of their length, to prevent extrusion of the packing. To insure perfect tightness the stem *F* was lapped to accurate form and a smooth finish.

When the valve is to be used at a temperature above the melting point of paraffin the packing can be protected from this temperature by using a very long valve stem with the packing at the top.

The valve may be secured by a nut *I* to a support *J*, or otherwise supported.

HEAD FOR A HIGH-PRESSURE CYLINDER.—Fig. 6 illustrates a suitable method of attaching an air-tight head to a cylinder designed to hold gas under high pressure, as for example the high-pressure purifiers of a

liquid air plant. The gasket *A* consists of a fiber ring placed in an annular grove in the head. The short sleeve *B* on the flange *C* not only increases the length of the thread but may be made to come close enough to the heads of the bolts *D* to prevent their turning when the nuts are screwed on. The bolts, flange and head should be of such strength that by screwing up the nuts a force can be applied equal to the sum of that exerted on the head by the gas and that required to make the gasket tight.

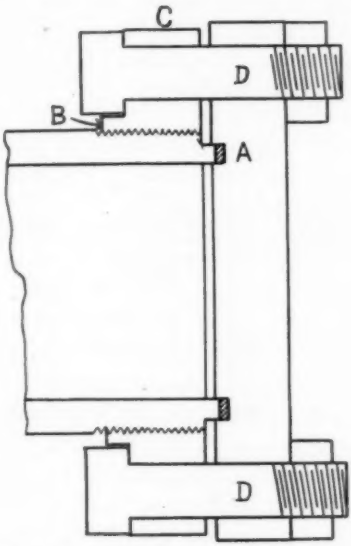

FIG. 6. *Head for a high-pressure cylinder.*

HIGH-PRESSURE UNIONS.—Fig. 7 shows a suitable design for a high-pressure union. This is made of brass and is made tight by applying sufficient force with the nut to slightly deform the metal at the contact surfaces. Unions made tight with fiber washers may also be used.

LIQUID AIR LEVEL GAGE.—It is sometimes desirable to be able to determine the level of the surface of liquid air or other liquefied gas in a place where it can not be seen. This can be accomplished by placing in a convenient position a glass U-tube containing a liquid and connecting one side of the tube to the space above the liquid and the other to a small tube entering the vessel from the side near the bottom. This tube is

usually extended into the vessel and its end turned down against the bottom of the vessel, but this does not appear to be necessary if the tube is not too large. If any liquid enters this tube it is partly vaporized by the heat conducted in from the outside, and the vapor produced drives the rest of the liquid out of the tube. Thereafter, a slow stream of vapor bubbles from the bottom of the tube and the pressure difference shown by the U-tube is then the hydrostatic pressure produced by the column of liquid in the vessel. The liquid used in the U-tube should not be water or any other volatile material, since its vapor would condense in the cold tubes and probably plug them. Glycerine is a suitable material. This gage is likely to be unsatisfactory if the liquid, or the vapor above it, is in violent motion.

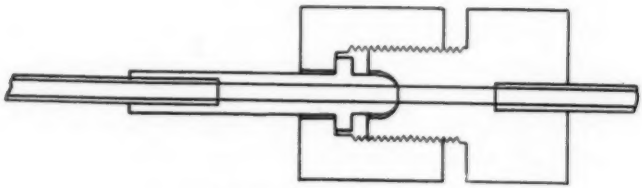

FIG. 7. *High-pressure union.*

Another form of gage consists of a float carrying an aluminum wire which extends through the top of the apparatus. The protruding portion of the wire may be enclosed in a glass tube to prevent the entrance or exit of gas.

HAZARDS.—It has already been pointed out, in the discussion of compressors, that only oil of very high flash point may be used in high-pressure air compressors, and that no oil whatever may be used in oxygen compressors. There must be at no point of a system containing compressed oxygen any oil of any kind. Very violent explosions may be produced by the presence of comparatively small quanti'ies of oil. This means that no storage cylinders, pipe lines or other equipment that have been previously used for other compressed gases should be used for compressed oxygen, since all other gases are compressed with the use of oil and the oil is likely to be sprayed into any equipment that the gas enters. Accidents have been caused by the use on a compressed oxygen line of an ordinary Bourdon gage that had been tested with oil.

In fact, compressed oxygen should be regarded as a very dangerous substance, and used with great precaution.

Oil explosions may be produced in air compressors or piping, even when the proper kind of oil is used, if too high a temperature is produced in the compressor, as the result for example of failure to turn on cooling water. Leaky exhaust valves and the presence of carbon deposit on valves seem to increase the danger. Other possible causes of explosion are the cleaning of valves or other parts with gasoline or kerosene and permitting the vapors to enter the compressor, or the presence of gasoline vapor or other combustible gas or vapor near the intake of compressor.

Danger to the eyes of operators is somewhat increased by employing high pressure gages with dials covered with glass. Mica or celluloid may be used. Gages are now made with faces of heavy metal and backs of thin metal, so that in case of explosion only the back fails.

All equipment constructed for use at high pressure should be tested under hydraulic pressure to a pressure considerably higher than that to be employed. Hand-operated hydraulic test pumps capable of producing pressures of several tons per square inch can be purchased.

Serious accidents have resulted from the use of liquid air to cool a bath of gasoline or other inflammable liquid. The evaporation of the liquid air produces nearly pure liquid oxygen, and the vapors of any inflammable liquid employed may be condensed in the liquid oxygen or form an explosive mixture with gaseous oxygen. An explosion may be produced, with the result that burning material is thrown upon the operator. In one fatal accident of this kind the apparatus was so constructed that it did not appear that the gasoline and the oxygen could come in contact and there was no known source of fire. There are several non-inflammable liquids that may be employed for low temperature baths within certain temperature ranges. These include carbon tetrachloride (freezing point $-22.9°C$), chloroform ($-63.5°$), methylene chloride ($-98°$), the eutectic mixture of 36 per cent tetrachloroethylene and 64 per cent carbon tetrachloride[34] ($-60.5°$), a solution of calcium chloride containing 29.8 per cent of $CaCl_2$ ($-55°$), and a 38 per cent solution of sulphuric acid, ($-75°$), though the corrosive properties of the last may be objectionable.[35] The inflammability of gasoline

[34] Hunter, U. S. Patent No. 1082528.

[35] An investigation to find suitable liquids of still lower freezing points is being made at the Bureau of Standards.

can be diminished or eliminated by the addition of carbon tetrachloride.

The practice of surrounding vacuum flasks containing liquid hydrogen with liquid air introduces a hazard of this character, since the breaking of a glass vacuum vessel appears to be capable of producing sparks and a powerfully explosive mixture of hydrogen and oxygen might be formed. The use of liquid nitrogen in place of liquid air would greatly diminish this hazard.

It is obvious that in any work with liquid hydrogen care should be used to avoid sources of fire. If induction motors can be employed in driving compressors or other equipment this avoids the sparks at brushes. The use of oil-immersion switches on such equipment avoids the chance of the ignition of an inflammable gas when a switch is opened. A jet of hydrogen escaping into the atmosphere can under some conditions become ignited as the result of becoming electrically charged by friction.

In some laboratories electrolytic generators are used for producing hydrogen and oxygen. An accidental reversal of current in such a generator delivers oxygen into the hydrogen supply and hydrogen into the oxygen. An attempt to compress either gas will then probably produce an explosion. Devastating explosions have been produced in this way in industrial plants. In one case, in which the electrolytic cells received current from a self-excited electric generator, a reversal of current was apparently produced by the influence of the counter electromotive force of the cells upon the electric generator. To avoid the possibility of such accidents the circuit should contain a circuit breaker of a type that will operate automatically if the polarity is reversed. Such circuit breakers can be purchased.

Many explosions have been caused by the accidental mingling of oxygen or air with a combustible gas in a gas holder, high-pressure cylinder or other equipment. The use of cylinders for other gases than those they are marked or intended to contain is a very dangerous practice. To diminish the chance of this being done accidentally or intentionally, different threads are usually used on the outlets of cylinders used for different gases. The threads usually employed in the United States are as follows:

Gas	Threads per inch	Outside diameter (inches)	
Hydrogen Helium	14	0.830	left straight U. S. standard thread.
Oxygen Nitrogen	14	0.895	right straight U S standard thread.
Acetylene	14	0.830	right straight U S. standard thread.
Carbon dioxide	14	0.843 (Eastern U S)	right straight U. S. standard thread.
	14	0.825 to 0.835 (Western U. S.)	right straight U.S. standard thread

BUREAU OF STANDARDS,
WASHINGTON, D. C.

Tests of Saha's Theory of Temperature Ionization made upon Caesium Vapor.—Saha's theory is, that in a gas of which the energy required to ionize an atom is eV, and which is at temperature T, the percentage of atoms ionized at any instant is the same as the percentage of dissociated molecules in a molecular gas if the work of dissociation per molecule is equal to eV. That is, ionization is regarded as completely equivalent to dissociation, and the same (universal) value of the chemical constant is considered to be valid for both processes. This is tested in H. A. Wilson's laboratory by measuring the conductivity of a Bunsen flame into which droplets of a caesium salt solution are being fed at a measured rate; this rate is the measure of the total number of caesium atoms per unit volume of the flame (the velocity of the flame gases being separately measured) and the conductivity is the measure of the number of free electrons or (presumably) ionized caesium atoms. The comparison of experiment with theory is carried out in a rather involved manner; the conductivity is measured for two values of vapor-concentration, at each temperature, and the temperature is calculated from these two data, assuming Saha's theorem to be correct; it is then compared with the actually measured temperature. In measuring the temperature by a pyrometric method it is assumed that the emission of the D lines (a sodium salt being introduced into the flame) is a purely thermal emission; so that two distinct assumptions are involved. In the two measurements characterized as "best" the calculated temperatures are 2030 and 2025°K, the observed ones are 2030° and 2000°K. Saha himself reports measurements on the conductivities of gaseous Cs, K and Rb at temperatures of the order of 1200°C and found that they stood in the order to be expected by his

theory. But the variation of conductivity with density at a fixed temperature does not agree with the theory; the number of electrons should vary as $\sqrt{d}$, the mean free path as $1/d$, the conductivity therefore as $1/\sqrt{d}$; but it was actually found to rise slowly with d. [B. T. Barnes, Rice Institute; Phys. Rev. *23*, pp. 178-188; 1924. M. N. Saha, Calcutta; Phil. Mag. *46*, pp. 534-543; 1923.]

K. K. DARROW

Change of Wave Length Occurring when X-Rays are Scattered by Carbon.—M. de Broglie has verified Compton's wave length shift by an experiment upon carbon. Primary rays from a Coolidge tube with tungsten target, excited by a voltage superior to the K excitation potential of tungsten, fall upon a secondary radiator consisting of powdered tungsten side by side with carbon. The rays from this radiator are dispersed and photographed with a crystal spectrograph; the K rays excited from the powdered tungsten by the primary beam (fluorescent rays) appear separated from the K rays scattered by the carbon, the displacement of the latter "corresponding in first approximation to the order of magnitude predicted by the theory of Compton and Debye" [M. de Broglie, Paris; C. R. *178*, p. 908; 1924].

K. K. DARROW

Kinetic Energy of Photoelectrons excited from the Incidence and Emergence Sides of a Sputtered Platinum Film.—Conventional method; the light was from a mercury arc and was dispersed by a Hilger monochromator; all transmitting windows and the support for the film were of quartz. The film was made of the proper thickness to give the greatest difference between quantities of photoelectrons from incidence and emergence sides, and the air-pressure adjusted to give the maximum quantities. The photoelectric currents do not approach zero asymptotically when the voltage is in the electron retarding sense and is made higher and higher; they become zero at particular values of voltage, and beyond these inverse currents are observed, due presumably to scattered light acting on the collector. But when using 2537A and supplementing the monochromator with a newly designed filtering solution cutting out all shorter wave light, Piersol found that the inverse currents are nearly suppressed and the photoelectric currents reach zero at about the same voltage for both the incidence side current and the emergence side current; and the same thing is observed when 1850A is used. It seems therefore that if monochromatic light carefully freed from shorter waves is used, the inverse currents will be avoided and the kinetic energy of the emitted electrons will be the same for both the cases. [R. J. Piersol, Pittsburgh; Phys. Rev. *23*, pp. 144-152; 1924.]

K. K. DARROW

ON A SIMPLE METHOD OF RECORDING THE TOTAL AND PARTIAL INTENSITIES OF SOLAR RADIATION

By Ladislaus Gorczyński

A simple form of recording pyrheliometer is obtained from the combination of a thermopile of the Moll type with a recording voltmeter of the Richard type. The large surface thermopile is composed of 80 elements made from thin strips of manganin and constantan, which are placed in a circle nearly 2 cm in diameter. These strips can be exposed to radiation over their whole length.

The thermopile in question affords a high degree of stability (absence of zero errors) and sensitivity, together with great quickness in action; namely, the time elapsing between the admission of radiation and the moment at which the full electromotive force is reached, is less than two seconds. The radiation from a candle at one meter distance yields about 90 microvolts.

Other details and some historical data are given.

With a recording voltmeter (type Richard) the large surface thermopile, properly diaphragmed and equatorially mounted (clock-driven), gives a new form of thermoelectric pyrheliometer, very rugged, and simple in use even for inexperienced observers. A solar radiation intensity of one gram-calory per minute per square centimeter of surface normal to the incident rays develops a current having an electromotive force of about 16 millivolts; this voltage is very nearly proportional to the intensity of the solar radiation so that the pyrheliometric records can be directly calibrated in g. cal. cm^{-2} $min.^{-1}$.

Some illustrations of the new pyrheliometer are given, with three sample records from measurements made by the author in the desert of Sahara. The method of obtaining the partial intensities by the use of colored glasses and liquid light filters, is also indicated.

Thermoelectric Method of Measuring Radiation

Independent of the ordinary thermometric method, the endeavors to apply the thermoelectric current to measurements of radiation date back several years. Special attention may be called to the old thermoelectric pyrheliometer constructed by Professor Crova and used at the University of Montpellier, France, in 1890. Among other forms we note especially the instrument of Féry, constructed in the beginning of the 20th century.

The difficulties which are met with in the application of thermopiles for measuring radiation, are principally the following.

(1) Constancy of the zero. The thermopile must be free from zero errors.

(2) Quickness in action. The ordinary thermopile is a rather slow instrument; when exposed to radiation a constant temperature will be obtained only after a considerable time; for instance, even in the best Rubens thermopile more than 15 seconds elapse before the full electromotive force caused by constant radiation is reached.

(3) High sensitivity. The sensitivity is generally not great enough to make possible the use of the ordinary millivoltmeters instead of the delicate mirror-galvanometers with photographic recording. However, when great sensibility has been obtained, it has been at the expense of the quickness.

(4) Rugged form of construction. The existing thermopiles were not sufficiently rugged for the comparatively rough handling they would meet with in practice for permanent solar radiation measurements.

Through the independent efforts in recent years of two distinguished physicists, excellent thermopiles have been constructed, which may be considered to have generally overcome the difficulties in the application of the thermoelectric method to continuous measurements of the solar radiation.

In consequence of these developments, on the one hand by Dr. Coblentz of the U. S. Bureau of Standards at Washington, and, on the other hand by Dr. W. J. Moll, lecturer on Physics at the University of Utrecht, new forms of thermoelectric pyrheliometers have recently been constructed. To this group of recent instruments, based on the use of the new American thermopile, belongs the excellent thermoelectric pyrheliometer constructed at Washington by Professor H. H. Kimball and Mr. E. H. Hobbs. On the other hand, on the basis of Dr. Moll's thermopile, a new form of thermoelectric recording pyrheliometer has recently been constructed in Europe and was used during my recent actinometric campaign in the Sahara desert. I give below a short description of this recording pyrheliometer, free from zero error, quick in action, very rugged in construction, and easy to work.

It seems that in the future only the simple thermoelectric method will be of current use, with the restriction, of course, that for control purposes special standard instruments (as for instance the water-flow pyrheliometer of Dr. Abbot) must always be recommended in view

of the necessary control and comparability of solar radiation measurements.

THE PRINCIPAL CHARACTERISTICS OF DR. MOLL'S THERMOPILES

The paramount object in the construction of these thermopiles is to minimize the heat-capacity of the active junctions and to give a maximum value to the passive ones.

The elements from which these thermopiles are made are extremely thin strips of manganin and constantan, soldered at *a* and *c* to copper bars (Fig. 1). These strips can be exposed to radiation over their entire length. The good heat-conduction between the junctions, and the small capacity of the junction *b*, causes practically an instantaneous equilibrium of temperature, in any case in less than two seconds.

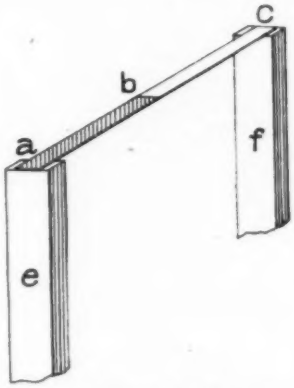

FIG. 1. *Element of Moll thermopile.*

The combination manganin-constantan, with a thermoelectric power of about 41 microvolts per 1°C, has been chosen chiefly on account of the high elastic quality of the two metals, which are soldered end to end and rolled out to the thinness of about 0.005 mm. Of importance is the durability of the metals, which neither rust nor corrode and also the fact that both manganin and constantan have a resistance which is independent of changes of temperature.

Fig. 2 is a sketch of the inner part of Moll's thermopile. *A* is a thick brass plate, in which flattened copper pins *B* have been clamped. A very thin coating of lacquer forms an insulating layer between these pins and the plate. The thermoelements, soldered on top of the pins,

consist of blackened metal strips of only about 5μ (0.005 mm) in thickness.

All this is sufficient for obtaining both quickness in action and constancy of zero. It is also an important advantage of this construction, that the temperature variations do not affect the thermo-electromotive force. An additional advantage is that it is not necessary to screen off the passive junctions; the elements can be exposed to radiation along their full length. Such elements may be combined for building up a linear, just as well as a surface, thermopile.

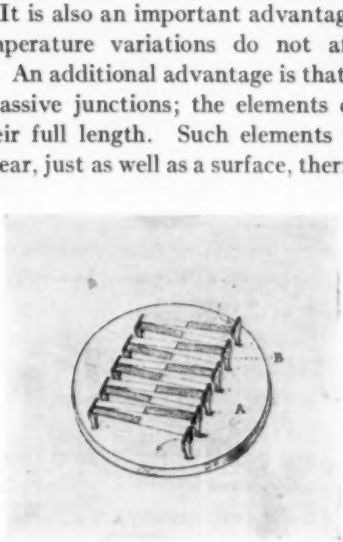

FIG. 2. *Interior view of Moll thermopile.*

The large surface-thermopile especially adapted for ordinary measurements of solar radiation intensity, is composed of 80 elements, arranged in three rows and placed in a circle nearly 2 cm in diameter (Fig. 3). The pile, with a resistance of about 45 ohms, is mounted in a solid cylinder, which is closed at one end by an ebonit plate with two terminals; and at the other end by a heavy brass lid, into which a protecting plate is fixed.

Instead of rock-salt or ordinary glass window, a plate of fluorite is now used which transmits all kinds of rays almost without absorption.

The large-surface thermopile of the Moll system gives about 90 microvolts from a candle at one meter distance. The microthermopile of 18 elements (suitable for spectral investigations when supplied with a special screen with a slit of variable width) gives about 25 microvolts under the same conditions. Both thermopiles are free from zero errors and combine in an exceptionally rugged form the two properties of great quickness in action with relatively high sensitivity.

THE NEW THERMOELECTRIC PYRHELIOMETER

It follows from the above that the application of the large Moll thermopile for measuring solar radiation gives not only a relatively high thermoelectric current (exceeding sometimes 30 millivolts even when diaphragms are used) but also permits of reaching the final values almost instantly. The problem of the direct and simple recording of the consecutive values of the solar radiation intensity even with the true and quick variations in the corresponding radiation (so frequent especially with cloudy sky) can now be considered as attained in a form convenient for general use.

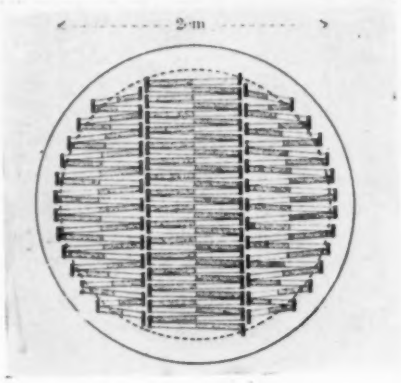

FIG. 3. *Large-surface Moll thermopile.*

The choice of an appropriate millivoltmeter for direct readings, and especially for automatic records, is an important question chiefly from the practical point of view. The millivoltmeter must not alter the good conditions of the sensitivity and quickness of the Moll thermopile; on the other hand, it is highly desirable that especially the recording millivoltmeter shall be of simple construction, such as the well-known types of Richard recording instruments.

It is certain that the improvement of many details necessitates—chiefly in electrical recording instruments such as millivoltmeters—a certain complication of the construction, as seen in certain new forms of recording voltmeters recently constructed in Europe and in the United States. But, on the other hand, it seems that the simplest form of these instruments is preferable for current use in solar radiation measure-

ments, which become in this manner suitable even for the less experienced observers.

The recording millivoltmeter of Richard, that I have chosen for use with the thermopile of the Moll system, is regularly built for ordinary industrial purposes. It has a resistance of 645 ohms and was used for my radiation measurements with two sensibilities (0-20 and 0-40 millivolts); the clock has two movements; 24 hours, and 52 minutes, for a complete revolution around the axis. The use of the 24 hour clock allows the observer to put the instrument in action during the whole day without the necessity of changing the record sheet during this period of time.

For the maintenance of the thermopile in a position permanently vertical to the solar rays, an equatorially mounted clock-driven arrangement is used. A special circle serves for the adjustment to the geographical latitude, and a level for the horizontal adjustment. For the quick north-south orientation of the instrument a magnetic needle can also be used.

Figs. 4 and 5 represent the general view of the thermoelectric recording pyrheliometer[1] and separately the diaphragmed thermopile equatorially mounted. Instead of a suspension with counter-weight, the thermopile may be installed directly on the clock-axis, with provision, however, for a small adjustment in order to follow the variations in the declination of the sun. This must be effected from time to time according to the season.

SOME PYRHELIOMETRIC RECORDS OF THE TOTAL AND PARTIAL INTENSITIES OF THE SOLAR RADIATION

Without entering into the details which concern more especially physical problems, we note that the voltage of the thermoelectric current generated in the thermopile when exposed to the solar rays can be considered as practically proportional to the radiation intensity. This simple relation enables us to convert directly into gram-calories per cm^2 and minute the values shown by a millivoltmeter. For this conversion it is necessary to previously obtain the reduction factor for the thermopile used with the corresponding diaphragms; this coefficient

[1] This recording pyrheliometer is regularly manufactured, and can be purchased at Etablissements de la Société Jules Richard, (Paris, 25 Rue Mélingue). The actual price is about $250, including the recording millivoltmeter and all the accessories. The recording millivoltmeter costs separately about $100.

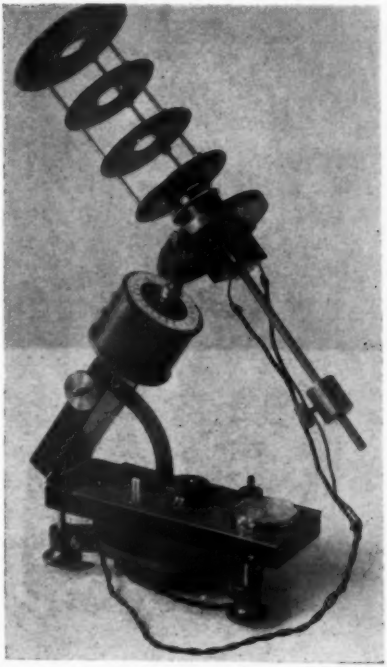

FIG. 4. *General view of recording pyrheliometer.*

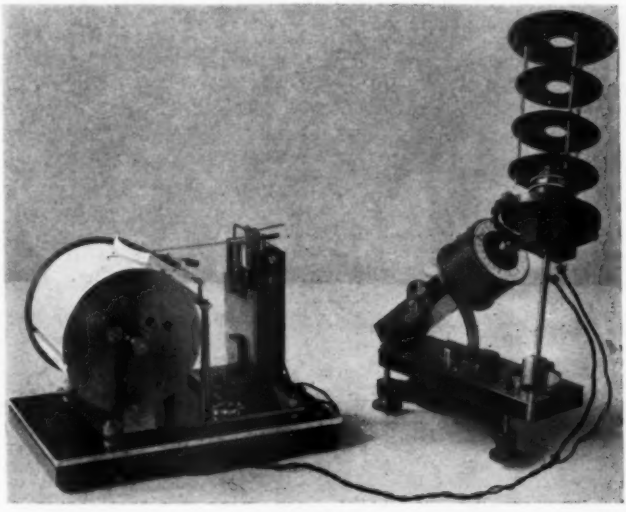

FIG. 5. *Thermopile with the diaphragms equatorially mounted.*

can be found either by comparisons with a standard pyrheliometer or by absolute determinations.

We note that with a solar radiation intensity of one gram-calory per minute per square centimeter of surface, the current generated by the large diaphragmed Moll thermopile has a voltage of about 16 millivolts. Besides the thermopile, the millivoltmeters must also be calibrated in order to determine the value of the current indicated by the position of the needle on the diagram. This is done by successively passing currents of 0 to 40 millivolts through the millivoltmeter coils.

Fig. 6 shows three examples of pyrheliometric records, obtained by me during the spring of 1924 in North Africa, namely, in the oasis of Touggourt, Desert of Sahara. Owing to the length of the diagrams, only a part of each record is reproduced here.

It follows from these records that even in the case of frequent passages of clouds the new recording pyrheliometer permits of obtaining good pyrheliograms, characteristic for the prevalent type of clouds, owing to the quick action of the thermopile. From these records the total amount of radiation, the diurnal march, and average values, can be obtained.

We note finally that not only the total radiation but also the partial intensities of the solar radiation can be easily recorded with the Moll thermopile. For this purpose special light-filters are used which are introduced (by means of a periodical swinging movement) before the aperture of the thermopile.

I have used principally four light-filters, viz:

(1) The so-called marmor-glass, opaque for visible rays but with a transmission up to 85% (for thickness of 7.3 mm) between 0.9 and 2.8μ.

(2) The red glass (Jena F. 4512, thickness 3.95 mm) with transmission up to 84% between 0.8 and 2.5μ, and opaque below 0.55μ and for the wave-lengths greater than 4.0μ.

(3) The yellow filters prepared by Dr. Moll from 5.16 gr. $K_2Cr_2O_7$ in 100 gr. H_2O. This liquid filter, in a cell of 11 mm thickness, transmits up to 98% between 0.7 and 1.2μ, decreasing to 0% for 1.5μ.

(4) The blue filter of 30 gr. $CuSO_4$ in 100 gr. H_2O; it transmits besides short wave-lengths also the radiation of long wave-lengths beginning at 1.8μ.

The use of the light-filters enables us to study, besides the variation of the total intensity, also the diurnal changes of the partial intensities of the solar radiation. The following extract from the measurements made in the spring of 1924 in the Desert of Sahara, shows some interest-

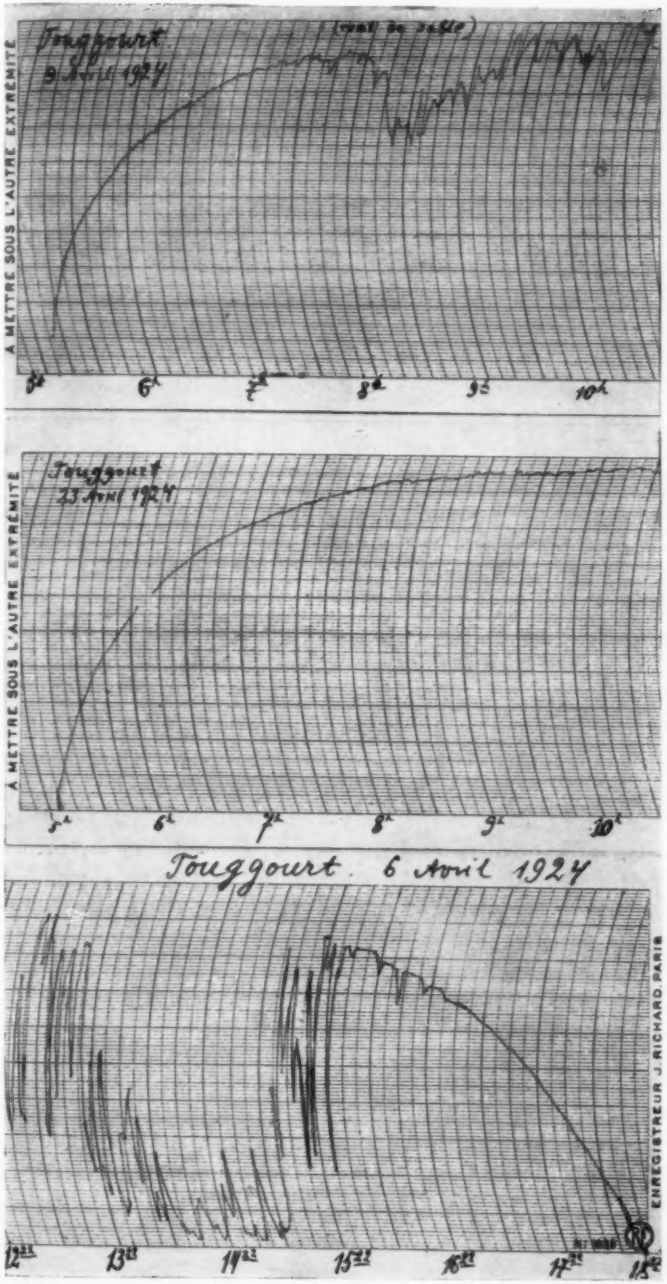

FIG. 6. *Pyrheliometer records obtained in the Desert of Sahara.*

ing changes in the percentages of the partial intensities in relation to the total intensity of the solar radiation.

MEASUREMENTS OF SOLAR RADIATION.
Oasis of Touggourt, March 28, 1924.
Time: Between 5:52 a.m. and 7:05 a.m.

Solar Zenith Distance.	Total Rad. Int. (Gr. cal, cm^2 min.)	Percentages		
		Red Infrared.	Infr.	Blue.
85½°	0.14	67	19	9
83°	0.25	62	18	10
80°	0.28	58	18	12
75°	0.37	54	17	15
71°	0.40	54	15	17

We see here the characteristic decrease from sunrise to noon of the proportion of the red and infrared rays, and at the same time the consecutive increase of the partial intensity of the solar spectrum.

CONCLUSION

From the considerations indicated above, it results that the new form of the recording thermoelectric pyrheliometer possesses in high degree the desired qualifications, namely, quickness of action, great sensitivity, and absence of zero error. On the other hand, the rugged construction of the thermopile, the simplicity of the whole instrument, and especially of the recording voltmeter, make the new pyrheliometer very easy for current use not only by the meteorological observatories but also by less experienced observers at the ordinary meteorological stations. The results already obtained in the desert regions of North Africa and in the plains of Europe, as well as the comparisons just made between this instrument and Marvin and Smithsonian pyrheliometers at Washington, D. C., show its convenience for use, and the practical adaptation of the measurements obtained with the new recording pyrheliometer in the different climates.

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A SENSITIVE MAGNETOMETER, INSENSITIVE TO EXTRANEOUS DISTURBANCES

By E. P. T. Tyndall

The use of a sensitive magnetometer in a Physical Laboratory or similar building is often rendered difficult on account of erratic disturbances due to varying stray magnetic fields from other apparatus in the building. The instrument here described is so designed as to be very little affected by such disturbances and at the same time to have great sensitivity. The simplest type of magnetometer uses as a controlling field the horizontal component of magnetic field at the suspended needle. Fluctuations in its direction or magnitude cause errors. By the use of a null method, in which the torque on the needle due to the specimen is balanced by a known torque due to current in a system of coils, errors due to fluctuations in intensity of the controlling field are eliminated, provided the direction of this field does not change. In the present instrument the control is due, to any desired extent, to an artificially applied field whose direction alone need stay constant. Moreover, it is possible to use the magnetometer in such a way that both poles of the specimen are effective, although the one pole method of Ewing can still be used where it is preferred.

The magnetometer needle is an approximately astatic pair of magnets on a single suspension. So far as the writer knows this device has never been applied to a magnetometer before and it has decided advantages as will appear below. The magnets are separated by a distance which for the two pole method mentioned above is equal approximately to the length of the specimen being tested. The instrument is represented diagramatically in Fig. 1; (a) is a cross section in an east and west plane, and (b) a section in a north and south plane. The two magnets, M_1 and M_2, are held in stirrups on the aluminum rod aa', which is suspended by a fibre, f. A small mirror is shown at g. The specimen is shown at CD as used in the two pole method. Other possible positions for it will be obvious. A permanent magnet or system of coils is placed in a suitable position to give the desired controlling field. The balancing coils are XY, ZW. The Gaugain-Helmholtz arrangement is used as it has obvious advantages. These four coils are connected in series in such a way that for a given current they all produce torque in the same sense on the suspended magnet system, and in

opposite sense to that produced by the two poles of the specimen. Adjustment of the current in the balancing coils until the spot of light reflected from g returns to its zero position constitutes a reading. From the dimensions of the apparatus and specimen and from the current in the coils, the magnetic constants of the specimen may be computed.

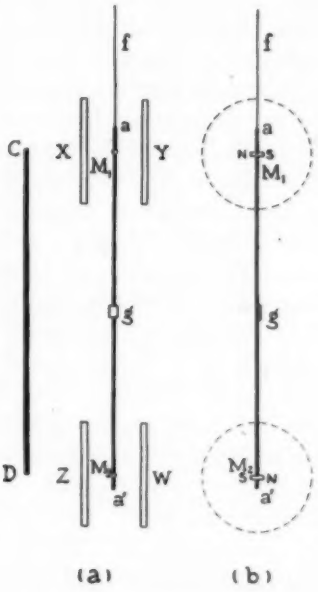


FIG. 1. *Diagram of magnetometer*
(a) Section in E-W plane
(b) Section in N-S plane

The possibility of freedom from disturbance combined with great sensitivity is easily seen. Refer to Fig. 2, in which the symbols have the following meaning:

M_1, M_2	Magnetic moments of magnets M_1 and M_2
H_0	Artificial controlling field, in fixed direction AB
H_e	Magnetic field at M_1, M_2, due to earth and undesired disturbances, a variable in direction and magnitude.
θ	Angle between H_e and AB at any instant.
$\Delta H_e, H'_e$	Components of H_e perpendicular and parallel, respectively, to AB.

H_1, H_2 fields at M_1, M_2, respectively, due to specimen.
H', H'' fields due to balancing coils XY, ZW, (Fig. 1), respectively.
Horizontal components of fields are meant.

For an accurate reading the axes of M_1 and M_2 must have the direction AB (i.e. this is the zero reading) when H' and H'' equal H_1 and H_2, respectively, regardless of the direction and magnitude of H_e. It is evident at once that changes in H_0 and H'_e have no disturbing effect. The disturbing torque due to ΔH_e is:

$$\Delta L = (\Delta H_e M_1 - \Delta H_e M_2)$$

This vanishes if two conditions are satisfied: (1) M_1 equals M_2; (2) ΔH_e is the same at M_1 and M_2. Satisfying the first condition is under the

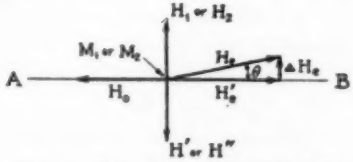


FIG. 2. *Fields acting at either M_1 or M_2.*

control of the experimenter. The second condition will be satisfied if the causes of disturbance are at a distance large in comparison with the distance between M_1 and M_2, a thing reasonably easy to achieve. In this second condition really lies the whole point of the method.

Great sensitivity is, of course, obtained by making $(H_0 - H'_e)$ vanishingly small. In general one may say that the desired effects on the magnetometer (torque due to specimen and opposite torque due to balancing coils) depend on the sum of M_1 and M_2 while the effect due to erratic disturbances depends on the difference of M_1 and M_2 and on the satisfaction of condition (2) above.

A trial instrument has been made. The magnets, M_1 and M_2 (Fig. 1) are of hardened steel 1 cm long and 2 mm in diameter. The aluminum rod, aa' is 1 mm in diameter and about 32 cm long. A silk fibre is used for suspending the system in a glass tube of 2 cm diameter. The magnets M_1 and M_2 are 30 cm apart. The radius of each balancing coil is 5.05 cm which is also the distance between the two coils of a pair. The controlling field has so far been produced by placing a permanent magnet with its axis parallel to M_2 and in the same horizontal plane. The control is then mostly on M_2 but there is no objection to this. Under these conditions a specimen of iron wire 0.305 g mass and 30 cm long, placed so that the distance CM_1 (Fig. 1) is 8.18 cm requires a current of

0.128 amperes in the balancing coils for a magnetizing field of 46.5 gauss. This is an induction in the specimen of about 15,070 units. With this sensitivity the zero position is very constant, the spot of light oscillating now and then two or three mm on either side of the zero position. This may be due to mechanical disturbances. How small this unsteadiness really is may be seen when it is noted that a current of 1 milliampere in the balancing coils will cause about a centimeter deflection.

The specimen is of course placed in suitable solenoidal windings for magnetizing, demagnetizing, and neutralizing vertical component of earth's field. The effects of the fields of these solenoids on the magnetometer are, as usual, balanced by other coils. Such coils need only be used at the same vertical level as one of the magnets, M_1 or M_2. No damping by vanes or other means is used, as a careful manipulation of the switch in the balancing coils circuit enables one to quickly stop oscillations. With a little practice, readings may be made with great rapidity.

It may be said in conclusion that the magnetometer design described above obliterates the chief objection to the magnetometric method, in that such a magnetometer may have great sensitivity without the corresponding liability to erratic disturbances. The advantage of this for certain types of magnetic work need hardly be pointed out.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF IOWA,
JUNE, 1924.

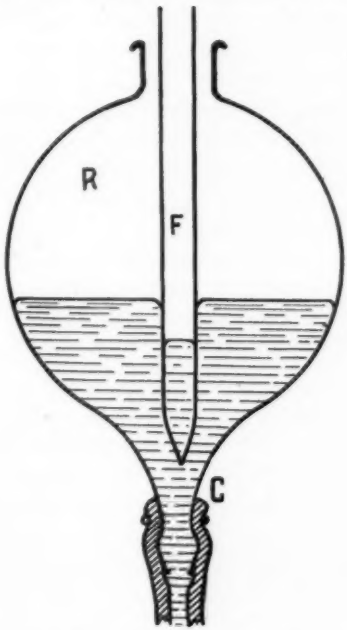
Direction of Ejection of Photoelectrons from Atoms by X-rays.—This is another piece of work performed with the C. T. R. Wilson expansion method, the ion trails being photographed simultaneously from two directions at right angles so that their absolute directions can be determined. The data consist of measurements on 163 tracks, in hydrogen gas; the author thinks, however, that most of the electrons responsible for them came from the oxygen atoms of the water vapor. The angle between track and x-ray beam is determined and a distribution function tabulated; it appears that the direction of maximum probability is inclined at 80° to 90° to the beam, that more than 85% of the electrons are ejected at angles between 45° and 115°, and that about twice as many tracks are inclined at angles $<90°$ as at angles $>90°$. Assuming that the entire momentum and energy of the quantum go to the electron, the author calculates a value 78° for the angle, close to the most probable value as observed; the deviations from this value are attributed to secondary causes. [P. Auger; C. R. *178*, pp. 929-931; 1924.]

K. K. DARROW

AN IMPROVEMENT FOR McLEOD GAGES

By E. L. Harrington

In most investigations involving the use of the McLeod gage it is desirable and in many it is absolutely essential that observations be made as quickly as possible in order to free the observer to give his attention to other observations being made in parallel with the pressure observations. Those experienced in such work know that the more one tries to hurry the longer it takes; the mercury will splash into the capillary and divide the air column, and even if this trouble is avoided successfully the mercury is bound to oscillate provokingly long.



The device shown in the figure has been found to eliminate both these troubles, and acts automatically. *R* is the mercury reservoir and may be connected by rubber tubing to the McLeod gage and lifted and lowered by hand, or it may be the fixed type and operated by air pressure; in the latter case the float would be wholly within the bulb. *F* is simply a short piece of glass tubing slightly larger than the outlet

of the bulb at C and drawn taperingly to a point as shown. F contains that amount of mercury which is found by trial correct to cause it to settle into the outlet at C the instant the mercury in the McLeod gage bulb approaches near to the capillary. This prevents the splash and cures the first mentioned trouble. But the fit at C will unlikely be mercury tight (it must not be) so that the mercury will continue to rise steadily to the point desired and may be stopped there without the usual wait for the oscillations to die down. As the mercury is lowered F floats out of the way and in no way impedes the flow of the mercury any more than it does as the mercury rises to fill the bulb proper. This is one device that eliminates certain troubles without introducing others.

UNIVERSITY OF SASKATCHEWAN,
SASKATOON, SASKATCHEWAN.

Critical Potentials of Excitation for Various Lines in the Spectra of He, Ne, Hg, Zn, Tl.—The question at issue is essentially this: Given a line emitted when the valence-electron of an atom falls from orbit B to orbit A, will it be excited by an impinging electron with just energy enough to lift the valence electron from its normal orbit (which may or may not be A) to orbit B? Or are there causes which prevent the valence electron from reaching B unless the atom is first ionized? To answer it, Hertz improved the conventional two-grid method of measuring resonance-potentials; he brought the first grid to within 0.5 mm of the filament, restricted the electron emission to a very small area of the filament (by spreading a narrow band of oxide upon the platinum) to insure emission from an equipotential surface, and went to the trouble of abolishing space charge from the field free region between the first and second grids by introducing easily ionized atoms into it to balance the electron space charge. In spite of all these precautions, the measured values of excitation potentials differed by 1.5 to 2 volts from the calculated values and Hertz's data consist essentially of statements of the *order* in which lines appear. This is in agreement with the first answer to the above stated question, and some beautiful photographs show how new lines appear suddenly with surprising brightness, when the accelerating voltage is increased only by a few tenths of a volt. The first lines to appear in the emission spectra of Tl and Zn vapors are also noted, and this method should prove a useful complement to existing ways of disentangling spectra.—[G. Hertz, Eindhoven; ZS. f. Phys., *22*, pp. 18-26; 1924.]

K. K. DARROW

A THERMIONIC BRAUN TUBE WITH ELECTROSTATIC FOCUSING

By L. T. Jones and H. G. Tasker

Ebert[1] was the first to suggest the use of the Braun tube to study wave form of electric and magnetic deflecting fields. The usual form, employing discharge between cold electrodes, involves cathode rays of too high a velocity to lend itself readily to general work. The sensibility of the cathode beam to deflecting fields is usually considered a function of only the velocity of the cathode beam. It will be noted in the following that there are exceptions.

The increasing number of uses [2] to which a Braun tube may be put has necessitated the development of tubes using thermionic emission in order to produce slow cathode rays of consequent high sensitivity. A number of such tubes have been described[3]. The characteristics of each are somewhat different and it will be seen that the tube here described may be operated under conditions that make its functioning unique.

The whole problem of a satisfactory tube lies in the definition of the spot on the screen and in the sensibility of the beam to deflection by electric and magnetic fields. It has been customary to focus the beam by an axial magnetic field. This is often disadvantageous since the resulting pattern on the screen is distorted and such distortion is inherent in the use of the magnetic field as a focusing device.

Focusing devices employing electrostatic methods have been mentioned by Wood and by Von Baeyer.[4] The tube developed by Hull depended upon the hole in the anode for the production of a small spot on the screen. Johnson advanced another step and is able to focus the beam by adjusting the filament temperature. This tube allows mercury vapor to remain after exhaustion and it is quite probable that the mercury vapor plays an important part in the focusing, as has been suggested, in addition to affording the electrons a path for ultimate return to the filament.

[1] Ann. d. Phys. u. Chem. *64*, p. 240.

[2] Gill, Electrician, *134*, p. 557; Wold and Stephenson, Phys. Rev. *21*, p. 706; DuFour, Comptes Rendus, *158*, p. 1339, 1914.

[3] Johnson, J. O. S. A. & R. S. I., *6*, p. 701, 1922; Bell System Tech. Jour., *1*, p. 142; Hull, Proc. Inst. Rad. Engr., *9*, p. 130; Wood, Phys. Soc. Lond., *35*, p. 109; Von Baeyer, Verh. d. D. Phys. Ges., *7*, p. 109; Engelhardt, Phys. Zeit., *24*, p. 239.

[4] loc. cit.

In the tube developed by the authors it will be seen that electrostatic focusing characteristics are present in addition to any effect that may be attributed to the presence of mercury vapor.

Fig. 1 shows the completed tube. Fig. 2 shows the schematic arrangement of the electrodes and the manner of operating the tube.

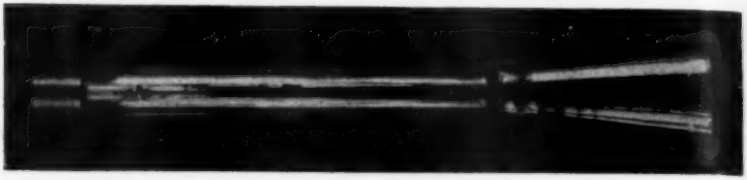


FIG. 1. *The completed tube.*

The cathode *C* consists of a disc of 1.5 cm diameter having a 2 mm hole through its center. The anode *A* is also pierced by a 2 mm hole and is placed about 2 cm in front of the cathode disc. The screen *S* is of calcium tungstate, very finely pulverized and deposited in ether, the ether being siphoned off. The oxide coated filament *F* is placed about

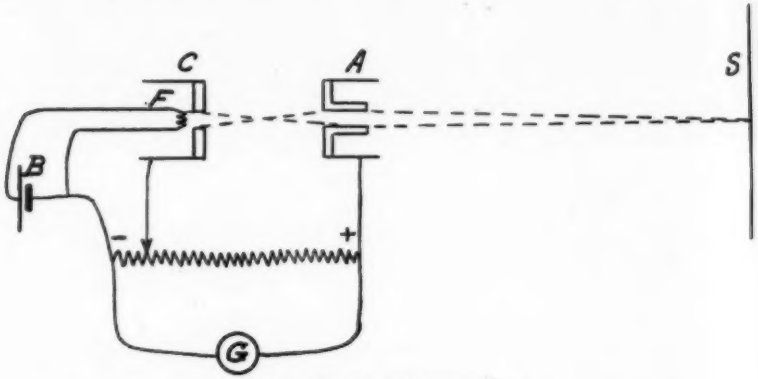


FIG. 2. *The schematic arrangement.*

.5 mm behind the cathode disc *C*. A small voltage, termed the exciting voltage and conveniently taken from the generator *G*, is applied between filament and cathode. The remainder of the voltage of the generator is applied between cathode and anode. An experimental tube was arranged with a movable filament. Neither anode nor filament distance need be exact but the value of the exciting voltage necessary to produce sharp focus with a given anode or driving voltage

is affected very greatly by changes in the filament-cathode distance. If the filament distance be made to approach zero no exciting voltage will be necessary to drive the electrons through the cathode disc and the tube will then exhibit the properties of that developed by Johnson. At a filament distance of .5 mm the exciting voltage will be less than 50 volts and slight alterations in this voltage will produce very marked changes in the size of the spot on the phosphorescent screen. A screen distance of 25 cm is usually used.

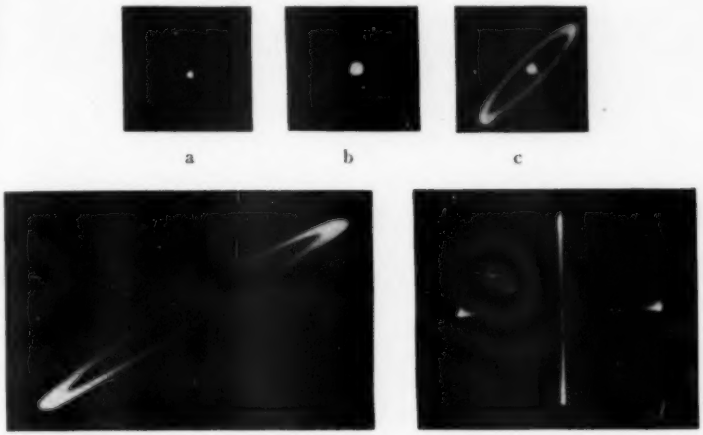


Fig. 3. *a, b, c, d, e. Actual size of figures on screen.*

The exciting voltage carries the electrons through the cathode disc and apparently through a "focus" a few millimeters in front of the cathode. The position of this focus is dependent on the exciting voltage, filament temperature and probably driving voltage. The driving voltage produces a "conjugate focus" at the screen. The electron paths probably cross at the first focus though this point has not been determined and it is not the intention to further investigate. Driving voltages above 300 volts are suitable.

The focusing characteristics of one particular tube are indicated in the data of Table 1.

It will be observed that for a given filament temperature, which may vary within quite wide limits, there are two (there are sometimes three) distinct values of the exciting voltage for which sharp focus of the spot on the screen is obtained. For intermediate values of the

exciting voltage the spot is very blurred. There are some indications that the different values of the exciting voltage bring different portions of the filament into focus. A tube with a *W* shaped filament was observed to have different portions of the *W* in focus for different values of the exciting voltage, the driving voltage remaining constant. The tube as at present used has the filament arranged to be nearly a point source.

TABLE I.

filament amps.	exciting volts	driving volts	spot diameter millimeters
1.30	25	200	1.5
1.30	60	200	1.5
1.30	10	500	1.5
1.30	20	500	1.5
1.50	55	500	1.5
1.15	10	1000	10.
1.15	100	1000	15.
1.30	35	1000	1.5
1.30	100	1000	10.
1.45	10	1000	1.5
1.45	85	1000	1.0

The tube is baked during exhaustion. Just before sealing from the pump a very considerable amount of mercury vapor is driven into the tube. The vapor pressure of mercury at room temperature (.0002 cm) affords just the correct amount of ionization for proper functioning of the tube. The spark equivalent of this vacuum is about 1 cm. In preliminary work one tube was arranged so that the mercury vapor could be removed after the seal-off and the focusing characteristics examined at increasing spark length equivalents of vacuum. As the vacuum increased the filament temperature necessary for sharp focus increased rather rapidly.

After prolonged use the cathode disc shows evidence of ionic bombardment. Data on the length of life of the tube have not been accumulated. The tube that had been longest in use, 50 hours, suffered accident while not in use. No tube has yet failed to function due to removal of the oxide coating by ionic bombardment.

The characteristics of the tubes have been observed to change with time and in rather irregular manner. The earlier tubes contained only the amount of mercury vapor present at the temperature of seal-off, 400° C. This vapor seemed to be gradually picked up by the brass electrodes and failure of the tube is then of an unexpected nature. The filament continues to emit but the tube loses almost entirely or entirely its ability to focus by means of the exciting voltage. In this case it seems beyond doubt that the electrons driven to the screen are secondary electrons formed at or very near the surface of the cathode disc *C*. The presence of such electrons has been shown by Engelhardt.[5] Those secondary electrons are uniform in velocity but since they originate outside the exciting field they cannot be focused by that field. One tube possessed characteristics such that the operator could at will produce a beam of either primary or secondary electrons merely by manipulating the beam by a magnet; the continued presence of the magnet was unnecessary.

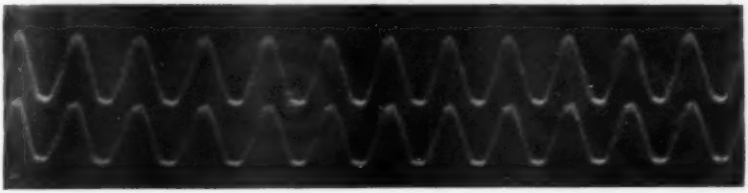


Fig. 4. *60 cycle wave due to external field.*

It is usual practice to deflect the electrons by an alternating electric field applied by plates placed outside the tube, the frequency being 1000 cycles or more. Fig. 4 shows a photograph taken at a frequency of about 60 cycles, the film being driven by a synchronous motor so that the path is retraced a number of times. The deflecting field was that due to 220 volts a.c. between plates placed 5 cm apart, outside the tube. It is worthy of note that a tube in which the electrons come from the filament seems to be not nearly so sensitive to this low frequency as one in which the electrons are secondary but of the same velocity; no reason is apparent.

Fig. 5 shows two 60 cycle sine waves, the deflections being due to an external field. The two traces were taken under identical conditions except that in the lower trace the filament temperature was such as to

[5] loc. cit.

cause copious emission while in the upper trace the filament temperature was reduced. All voltages remained constant. With a low frequency alternating electric field applied externally the maximum deflection may be altered at will, having any value from zero to the

FIG. 5. *Increased deflection for reduced filament temperature.*

radius of the screen, by merely altering the filament temperature. Since the same effect may be accomplished by altering exciting voltage (which is a small portion of the total) it is apparent that for some reason as yet unexplained the deflection is a function of the number of electrons in the beam. The breadth of the beam striking the anode A is greater than the diameter of the hole in the anode, for most values of the exciting voltage. This breadth is altered by changes in that voltage and hence altering the exciting voltage alters the number of electrons passing through the anode.

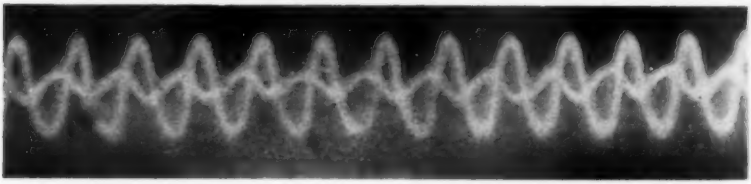


FIG. 6. *Deflections due to internal and external fields. Internal is the larger.*

When the deflecting plates are placed inside the tube the deflection is a function of the velocity alone and is not dependent on filament temperature or exciting voltage. Fig. 6 shows two 60 cycle waves superposed. The larger amplitude is due to internal plates the

smaller due to an external field. Fig. 7 shows two traces taken under the identical conditions of Fig. 6 except that in Fig. 7 the filament temperature was lowered. The smaller amplitude, due to the internal field, is seen to equal that of Fig. 6 while the amplitude due to the external field has been greatly increased.

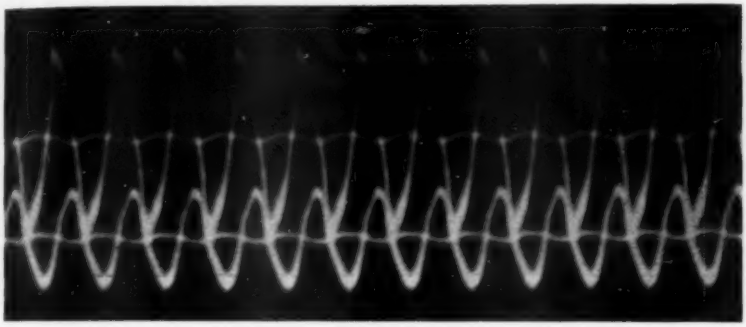


FIG. 7. *Deflections due to internal and external fields at reduced filament temperature. Internal field deflection is the same magnitude as in Fig. 6.*

Fig. 8 shows the wave form obtained from a small transformer. The upper trace is taken with internal plates and the lower with an external field. Other conditions were identical.

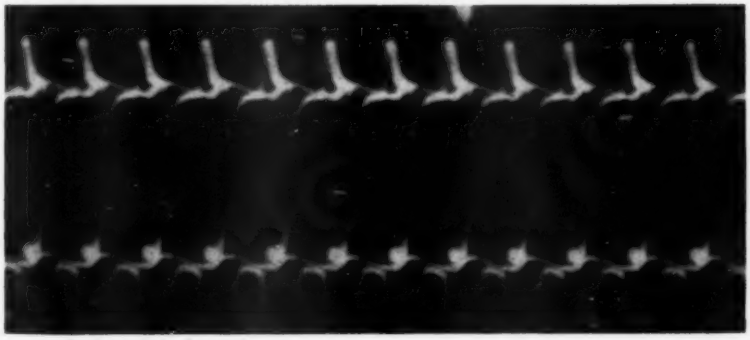


FIG. 8. *Waves from small transformer by internal and external fields.*

Fig. 9 shows a photograph taken by a film that was given a translatory as well as a rotary motion. The path was thus not retraced. The photograph indicates the intensity of the spot on the phosphorescent screen.

It is apparent from the preceding that the thermionic Braun tube is not reliable as an oscillograph for external electric fields of low frequency. Whether this peculiarity persists when the deflecting frequency is large will be determined in some future experimental work and must be left for a later paper.

FIG. 9. *Intensity of spot on screen shown by film exposed "once over."*

The authors are indebted to Drs. T. S. Taylor and F. B. Jewett for oxide coated filament and to Dr. W. D. Coolidge for tungsten cathodes used in preliminary work with this tube.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

Ionization of the Vapors $HgCl_2$ and HgI_2.—These experiments are by the exact method of H. D. Smyth, apparently independently but not so thoroughly developed; that is, the ions are produced by electron bombardment of a stream of vapor shooting transversely across the electron stream from an evaporating deposit of salt to a condensing chamber, and the charge-mass ratio of the ions is measured by the magnetic deflection method in an auxiliary chamber. Negative ions of about the mass of the chlorine or the iodine atom, respectively, are observed; these ions appear only when the electron accelerating potential exceeds some 12 volts, in the case of HgI_2 vapor. The beam of negative ions seems to be very homogeneous in speed, yet the calculated values of mass deviate by 10-20% from the true masses of the atoms in question: probably on account of magnetic leakage. When a beam of the positive ions is admitted to the deflection chamber it is subdivided into various pencils, some of which probably consist of HgI_2+ and $HgI+$ ions. The evidence therefore, so far as it goes, indicates that ionization of these molecules consists in splitting the molecule into two oppositely charged atoms or atom groups, just as in electrolysis—not in freeing an electron.—[V. Kondratjeff and N. Semenoff: ZS. f. Phys., *22*, pp. 1-8; 1924.] K. K. DARROW

DEMAGNETIZATION AND HYSTERESIS LOOPS

By L. W. McKeehan and P. P. Cioffi

Magnetic measurements are frequently vitiated by imperfect demagnetization of the specimens used. This cause of error is so obvious in hard magnetic materials that it is rarely overlooked in studies of their properties. That it is relatively just as important in the case of soft materials is not so apparent. It will be of interest, therefore, to describe some of the results which we have obtained in this connection during work on the properties of permalloy[1], in which straight wires and tapes were used. In the methods already described by one of us[2] for checking the demagnetization, advantage was taken of the fact that initial permeability is a maximum if demagnetization has been complete. Higher accuracy is afforded by the modifications in procedure here presented, and some additional light has been thrown upon the nature of demagnetization by alternating magnetic fields. In order to avoid repetitions it will be stated at once that all the experimental details are here the same as those described in the previous paper[2].

The curves A, B, C and D in Fig. 1 show how advantageous it is to increase the increment of applied field to such a value that the permeability, μ_Δ, becomes about twice its initial value, μ_0, the maximum at exact demagnetization being made much sharper by this change in ΔH. In order that the larger values of ΔH should introduce no uncertainty into the value of applied compensating field H_a at which the value of μ_Δ is a maximum, the procedure in these measurements was as follows. The compensating field H_a was first established; the alternating demagnetizing field was next applied and reduced as smoothly as possible to zero. The resistance in series with a second magnetizing winding was then adjusted so that closing the circuit through this winding added or subtracted a field half as great as the desired increment ΔH. A reversing switch in this circuit was now operated several times, the applied field varying accordingly between $H_a - \frac{\Delta H}{2}$ and $H_a + \frac{\Delta H}{2}$. Finally a galvanometer deflection was taken for a single reversal in one direction or the other, and the corresponding value of $\mu_\Delta = \frac{\Delta B}{\Delta H}$ was computed.

[1] H. D. Arnold and G. W. Elmen, Frank. Inst., J., *195*, pp. 623-632, 1923.
[2] P. P. Cioffi, J. O. S. A. and R. S. I. *9*, pp. 53-60; 1924.

FIG. 1. *Dependence of permeability upon demagnetization.*

If ΔH is made so large that saturation is approached too closely at each end of the cyclic process just described, the accuracy of compensation diminishes, as is seen by comparing curve E with curve D. In any case H_a at the maximum is equal in magnitude and opposite in sign to the vertical component H_0 which existed before its application and which it just compensates at this point.

The results presented in Fig. 1 may be thought of as giving in μ_Δ the mean slope of narrow hysteresis loops centered at H_a. The complicated shape of some of the curves suggested that a detailed study of entire hysteresis loops might throw more light on the effect of demagnetization at various values of H. Selected loops illustrating a variety of facts disclosed by such a study are shown in Figs. 2, 3, 4 and 5, the loops of each figure having the same range in H. Although hysteresis losses in permalloy are very small its magnetic characteristics are so permanent under proper treatment that the material offers exceptional advantages for such a study of hysteresis.

The permeability μ_Δ is a mean value for the whole loop of width ΔH. To emphasize this fact a line has been drawn between the tips of each loop, and its slope $\bar{\mu}$ has been given for each case. It should be noted that the large measured changes in B made the ballistic measurements as easy and as precise in the case of these narrow loops as in the case of much wider loops, involving enormously greater energy losses, in harder magnetic materials. For a comparison between the hysteresis in a particular sample of permalloy and that in magnetic iron see Fig. 6 in the paper by Arnold and Elmen[1]. The method for flux measurement being purely differential no attempt has been made to estimate the true remanences, and the various loops have accordingly been plotted with arbitrary origins for B so chosen that the range in B covered by the loop is divided by the line $B=0$ in the same ratio as is the range in H by that value of H at which the demagnetizing process was applied. The point at which demagnetization was effected must, therefore, fall on a line joining the tips of the loop, and is marked in each case with a small circle. The scale for H gives partially corrected values, the applied fields, H_a, being greater than the plotted abscissae by the amount, $-H_0$, which compensated the vertical component of the earth's field, determined at frequent intervals in the manner described above. The values of H have not, however, been corrected for the induced and residual magnetization of the wires. The experimental points are shown on each curve and it will be noted that in all except one case both sides of each loop have been determined. The single excepted case

has been assumed to give a symmetrical loop. The conclusions derived from a study of these and similar curves are given below.

The first point to be emphasized is the great similarity between loops *F* and *G* of Fig. 2 and that between the corresponding wider loops *K*

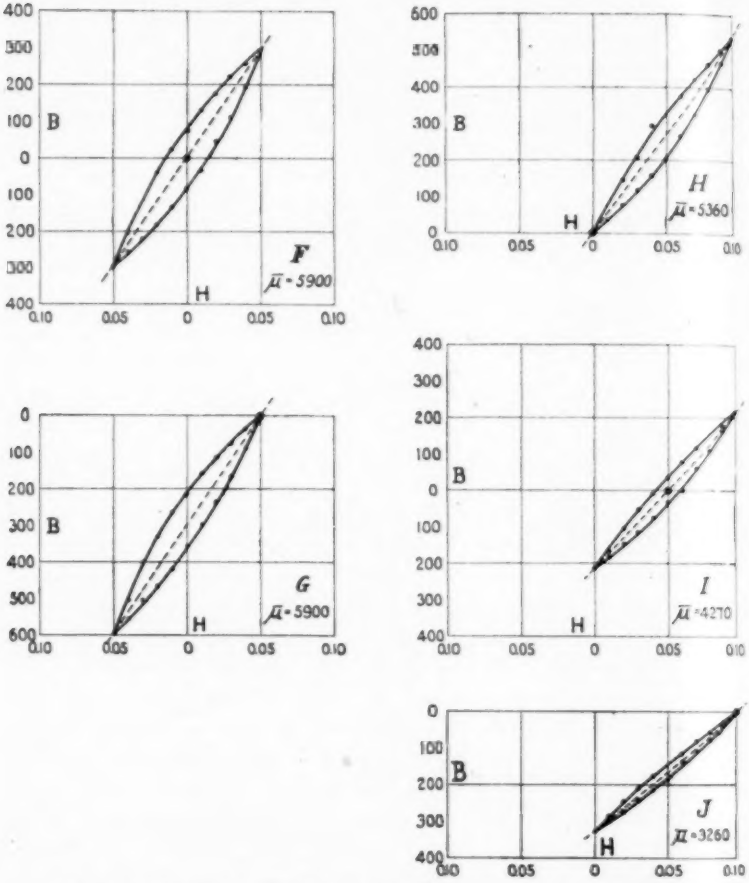


FIG. 2. *Dependence of loop shape and area upon demagnetization. Narrow loops.*

and *L* of Fig. 3. In *F* and *K* the demagnetizing process was applied at the center of the loop and in *G* and *L* at the upper tip, as indicated in the figures. The lack of difference in results means that a few reversals of the uncompensated field existing at the time of demagnetiza-

tion is effective in destroying the magnetization which was in equilibrium with this field during the demagnetizing process itself.

The second point of interest is shown by the two series, H, I and J of Fig. 2, and M, N and O, of Fig. 3. Each series consists of loops taken

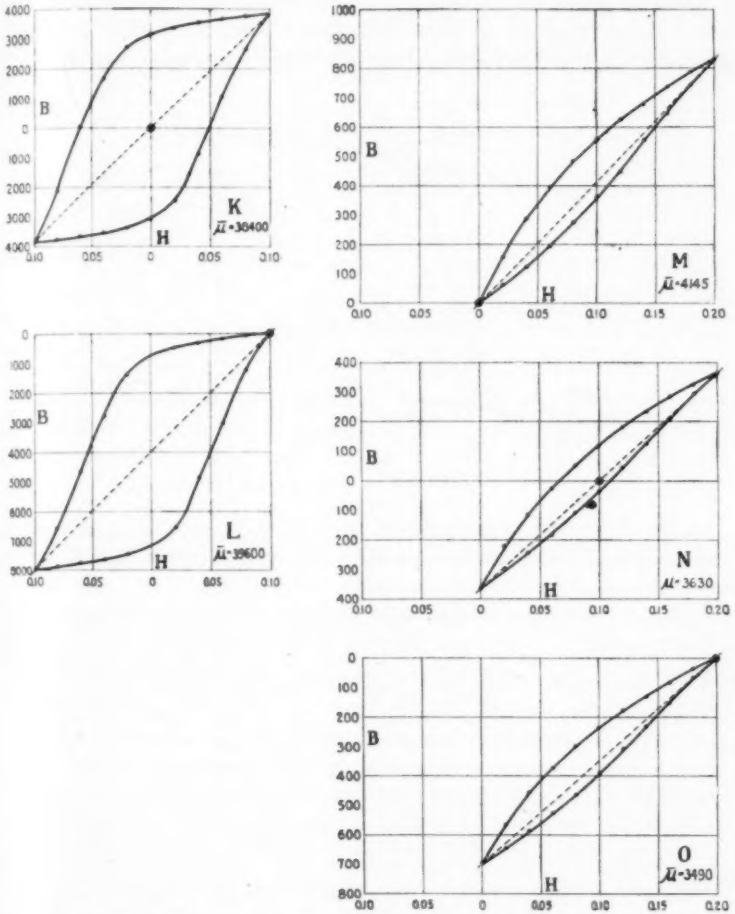


FIG. 3. *Dependence of loop shape and area upon demagnetization. Wider loops.*

between the same limits in H but with progressive increase in the value of H at which the demagnetizing process was applied. Unlike the loops G and L discussed in the preceding paragraph the second and third members of each series do not extend far enough in the negative direc-

tion to reverse the field existing at the time of magnetization and the progressive decrease in $\bar{\mu}$ shows that this prevents some of the elements not originally demagnetized from contributing to the measured changes in flux.

The decrease in $\bar{\mu}$ in passing from F to I and from K to N is, of course, merely a confirmation of the results shown more completely in Fig. 1, and is fully accounted for by changes in remanent magnetization.

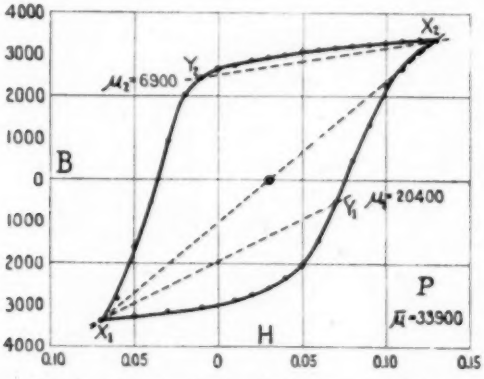


FIG. 4. *Second method for checking demagnetization*

All the loops which correspond to ineffective demagnetization are unsymmetrical[3], and the dissymmetry increases with the width of the loop and with the increase in the mean value of H. This is well shown by some of the figures already discussed and, for larger changes in B, by curve P, Fig. 4 and curve Q, Fig. 5. This dissymmetry suggested another method for checking the compensation of a stray field. After a demagnetizing process, which need not be especially effective, a cyclic state is established by several traversals of a fairly wide loop between equal positive and negative field increments. The mean permeability over about half of the total range in flux is then measured from each end of this loop in turn, as illustrated at X_1 Y_1 and X_2 Y_2, Fig. 4, using the same change in H in both cases (0.14 gauss in the illustration) and executing a few stabilizing reversals between the two measurements. Unless $\bar{\mu}_1 = \bar{\mu}_2$ the loop is proven unsymmetrical

[3] A. W. Smith and H. E. Hammond, Phys. Rev. (2) *15*, pp. 249-255; 1920, show unsymmetrical loops for soft iron, cast steel and cast iron which are similar in general features to those here obtained. It seems doubtful from our experiments, however, whether, as they suggest, either branch of an unsymmetrical loop coincides exactly with any part of a symmetrical loop.

and the appropriate direction of change in compensating field is at once apparent. Field fluctuations which may occur during demagnetization or between ballistic measurements are rather less troublesome in this method than in that which employs only a small range in H.

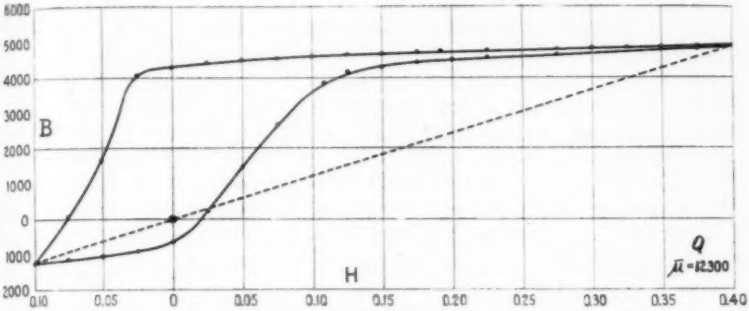


FIG. 5. *Wide loop showing great dissymetry*

All the data here presented were obtained with one carefully annealed permalloy strip under no tension. The numerical results, of course, apply only to this particular piece, although they are fairly representative of a wide range of samples.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED
MARCH 5, 1924

The Phonic Chronometer.—A twelve page description with diagrams and photographs is given a high speed, tuning fork controlled, chronometer which has been used for sound-ranging, depth sounding, psychological measurements, automobile speed events and the like. The tuning fork is used to maintain accurately constant the speed of a rotating drum through the agency of a specially designed high torque phonic motor of which only a brief description is given. The recording dial has a low moment of inertia and makes frictional contact either with the constant speed drum or a brake, the movement from one to the other being effected by means of a differential magnet controlled by the event to be timed. The starting and stopping errors which are opposite in their effects can be adjusted to compensate each other and have actually been reduced to less than a thousandth of a second. The authors have found a new form of contact desirable for the tuning fork and have been able to maintain the frequency of the fork constant to .01%, over a very considerable time interval.—[A. B. Wood and J. M. Ford. Jour. of Sci. Inst., *7*, pp. 161-173; March 1924.]

L. BEHR

Application of the Weber-Fechner Law to Photometry.—A problem in photometry consists in giving the photometric field such form, dimensions, and distance that the two intensities of illumination, I and $I+\Delta I$, have a difference ΔI as small as possible. The errors of observation will be less than ΔI because equal or larger errors will be perceived by the eye.

The fundamental problem of photometry reduces itself to finding the ratio of $I+\Delta I$ to I for different experimental conditions.

Weber and Fechner found that $(I+\Delta I)/I = \text{constant}$ and $\Delta I/I = \text{constant} = K_1$. But this law breaks down for very low and for very high intensities. The formula indicates that if the intensity in one part of the field were zero there would be no excitation. We know however that the limit is not zero. Fechner tried to correct the formula by assuming that the value of I was not due entirely to the exterior illumination but in part to a subjective luminous sensation such as might be caused by the decomposition of sensitive pigment in the retina. This assumption gives $\Delta I/(I+a) = \text{constant} = K_2$. The formula does not yet agree with the experimental facts. Helmholtz has shown that the sensation depends also on the visual field subtended by the area of given intensity. He proposed the following generalization.

$$\Delta I \int_0^s \frac{ds}{I+a} = \text{constant} = K .$$

The results of Konig and Brodhun were in agreement with this theory.

The present writer has carried out experiments to verify the further conclusions from Helmholtz's theory. If the intensity I is considerable in comparison to a the formula becomes

$$\Delta I \int_0^s \frac{ds}{I+a} = \frac{\Delta I}{I} \int_0^s ds = \frac{\Delta I}{I} s = K$$

In consequence a hyperbolic relation should exist between $\Delta I/I$ and s. It was found that such was not the case but that

$$\frac{\Delta I}{I} \cdot s = \varphi(s) = K_0 + K's$$

represented the facts very closely.

Experiments were made to determine the effect of distance of the photometric field. If the dimensions of the visual field are considerable the precision of measurement is not a simple function of the angular field because the light a has different values in the illuminated portions of the retina.

With a point source Helmholtz's fundamental equation becomes $\Delta I\sigma/(I+a) = \text{constant} = K$, where σ is a constant that corresponds to the retinal image of a luminous point.

The time used in making a photometric match with point sources, such as stars, was also considered and the error found to be somewhat less when the time was rather short.—[M. P. Lasareff, Revue d'Optique, 3, pp. 65-70; 1924.]

G. W. MOFFITT

PHOTOMECHANICAL WAVE ANALYSER APPLIED TO INHARMONIC ANALYSIS

By C. F. Sacia

Recently there arose the necessity of obtaining analyses of a large number of oscillograms of spoken vowel sounds.[1] The usual methods of harmonic analysis could not be applied in this case, for a complete analysis of each wave form was desired. This led to the development of the apparatus and method here described. For the sake of clarity, this description is preceded by a brief review of the principles of Fourier Analysis.

The resolution of a wave form (or any function) into its sinusoidal components is termed Fourier Analysis: if the wave form is periodic the operation is harmonic analysis; if it is aperiodic, this resolution may be called "inharmonic" analysis. The distinguishing property of a periodic function is that it consists of cyclic forms which are all alike and infinite in number, the duration of the function being from $-\infty$ to ∞. A function which has this property with the exception that its duration is from 0 to ∞ (i.e., it vanishes in the range $-\infty$ to 0) is of general use in classical theory of vibrations and is a quasi-periodic function. An aperiodic function, on the other hand is any other kind of function not included in the above two classes. Nevertheless, it is often legitimate to deviate slightly from these definitions when considering functions which endure for a considerable length of time and whose cyclic forms do not change much. Such functions are thought of as being periodic, as in the case of a cyclic force acting upon a vibratory system having dissipation or damping sufficient to considerably abate, within a short interval of time, the response to the force at a given instant. For example, a vowel sound of moderate duration and uniformity affects one's ear at various instants just as though it were truly periodic, although its effect upon an instrument of small damping might be far different. For analytical purposes, however, the definitions are adhered to more closely.

A periodic function is represented by a Fourier series while an aperiodic function is analogously represented by a Fourier integral.

[1] Bell System Technical Journal, April 1924: Crandall and Sacia, "A Dynamical Study of the Vowel Sounds."

The functions under consideration, vanish outside a given range T so that

$$F(t) \equiv \frac{1}{\pi} \int_0^{\infty} d\omega \int_{-T/2}^{T/2} F(\lambda) \cos \omega (t-\lambda) d\lambda \tag{1}$$

where $\omega \equiv 2\pi$ times frequency. This may also be written

$$F(t) \equiv \int_0^{\infty} d\omega \left\{ \left[\frac{1}{\pi} \int_{-T/2}^{T/2} F(\lambda) \cos \omega \lambda \, d\lambda \right] \cos \omega t + \left[\frac{1}{\pi} \int_{-T/2}^{T/2} F(\lambda) \sin \omega \lambda \, d\lambda \right] \sin \omega t \right\}. \tag{2}$$

The Fourier Series

$$\Phi(t) \equiv \sum_{n=1}^{\infty} \left\{ \left[\frac{2}{T} \int_{-T/2}^{T/2} \Phi(\lambda) \cos n\omega_0 \lambda \, d\lambda \right] \cos n\omega_0 t + \left[\frac{2}{T} \int_{-T/2}^{T/2} \Phi(\lambda) \sin n\omega_0 \lambda \, d\lambda \right] \sin n\omega_0 t \right\}, \tag{3}$$

where $\omega_0 \equiv 2\pi/T$, represents a periodic function. A comparison of (2) and (3) shows the following points of distinction.

Periodic Function	Aperiodic Function
Components are finite magnitudes.	Components are in general infinitesimals
There is only a finite number of components in a finite frequency range.	There is an infinite number of components in a finite frequency range.

The root-sum-square of the two integrals with respect to λ is the amplitude of the component for the corresponding frequency. A diagramatic representation of these magnitudes for all frequencies is shown by a series of vertical lines spaced as regular frequency intervals in the case of the periodic function, and by a continuous curve, whose ordinates are the coefficients of the infinitesimal $d\omega$, in the case of the aperiodic function. The former is a line spectrum and the latter a band spectrum. Spectra of waves or functions which are defined mathematically can be computed from equations (2) and (3). Fig. 1 shows the band spectrum for frequencies up to 300 cycles of a simple wave of

two pulses, and Fig. 2, the spectrum of a somewhat similar wave of 6 pulses, while Fig. 3 shows the line spectrum of a periodic function of an infinite number of these pulses. The relation between all three figures gives an illustration of the following more general principle.

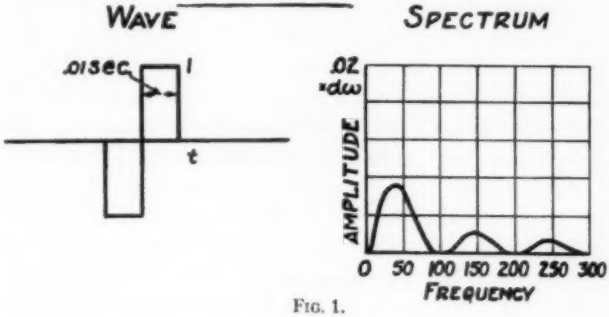


FIG. 1.

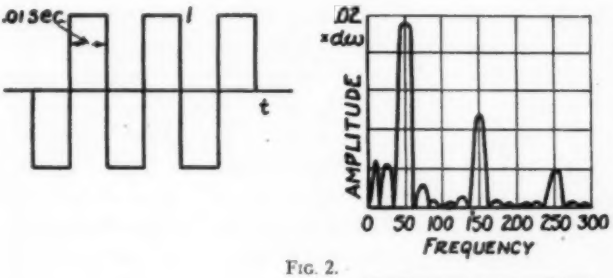


FIG. 2.

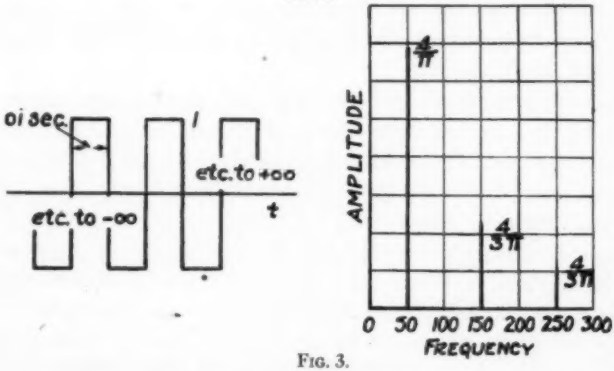


FIG. 3.

Consider the periodic function generated by the continual repetition of any aperiodic function $F(t)$. Its Fourier series is given by equation

(3) since $\phi(t) = F(t)$ *within the limits of* $-\frac{1}{2}T$ *to* $\frac{1}{2}T$. Thus the effect of the repetition is to build up the infinitesimal components into components of finite amplitude for only those frequencies which are integral multiples of the frequency of repetition $1/T$ and to neutralize or suppress the components of all other frequencies. Fig. 2 illustrates a step in this process. (In this case the even harmonics are also suppressed). The analogy between equations (2) and (3) shows how simply the components of the generated function determine a set of components in $F(t)$. If, now, the period of repetition be increased, a different periodic function is generated and its components determine another set of components in $F(t)$. In this way, as many points on the spectrum as are desired can be determined, but if the line spectrum of the generated wave is of great density, one setting of the period of repetition yields a set of components which determine the spectrum with sufficient accuracy. Such is the principle upon which the photomechanical analyser depends for performing the inharmonic analysis of an aperiodic wave, i.e., by means of the harmonic analysis of the generated wave. Although the number of repetitions is not infinite, only a short time is required to make it large enough to have the same effect upon the tuned part of the apparatus.

The photomechanical analyser operates according to the following scheme. (1) The wave form is reproduced as a fluctuating beam of light whose cross-sectional area varies with time in accordance with the original wave. (2) Corresponding electric vibrations are derived from the light variations by means of a selenium cell, photoelectric cell, or other suitable device. (3) From these vibrations, the various components are selected for measurement, the calibration of the apparatus being taken into account.

In order to accomplish the first step, the wave is represented as a black profile on a narrow transparent strip, the ends of which are joined to form an endless belt. Mounted on pulleys, this strip is driven at a regulated speed, while an optical system throws upon the strip an image of a uniformly illuminated slit. The transmitted beam is thus varied in cross-sectional length, hence its total light flux varies according to the original wave form. Diagrams of the apparatus so used are shown in figures 4 and 5. The source of light was a Pointolite, which was mounted below the bench for economy of space. Because of the stigmatic combination of cylindrical and spherical lenses, the light image on the cell remains fixed in size, shape, and position: it varies only in intensity as the moving strip varies the cross-section of the

beam. Nearly the whole of the useful surface of the cell is thus covered by the light. In order that there be practically uniform illumination over the operating length of the slit (2 cm) its distance from the light

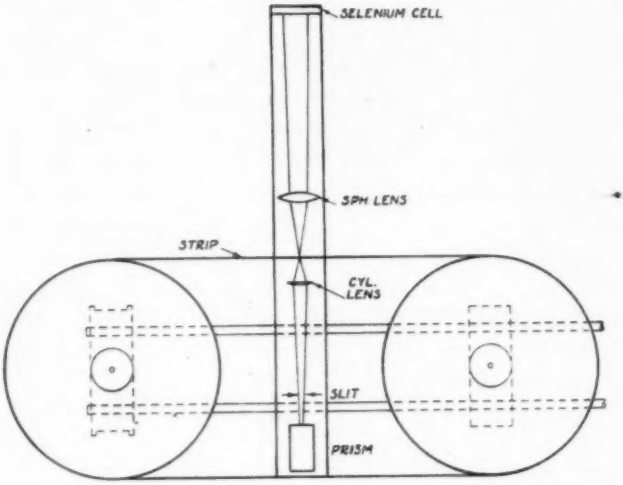


FIG. 4. *Plan of apparatus.*

source was made 20 cm. The width of the slit is 0.015 cm, distance from the cylindrical lens 9 cm and distance from lens to the strip 2.3 cm.

The pulleys were driven by a DC motor originally rated at 0.1 HP, 110 volts, 1100 RPM. In order to keep its speed free as possible from

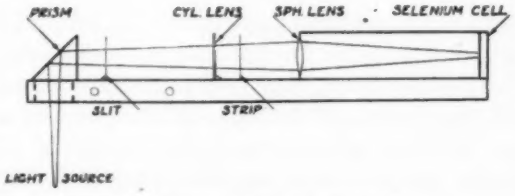


FIG. 5. *Elevation of optical bench.*

fluctuations due to unsteady line voltage, to the armature teeth, and to variable brush contact resistance, the following precautions were taken. The field was rewound for excitation by a 12 volt storage battery, while

the armature was run from a battery of 1.5 volts large dry cells. A flywheel was mounted on the shaft, and the brushes were snugly secured in their holders, their contact surfaces then being ground to accurately fit the commutator. As a result, the speed, once set, remained constant to within less than 1 per cent. For a closer adjustment in speed setting than could be obtained by the 1.5 volt steps, use was made of a 2 volt storage battery shunted by a 50 ohm slide wire potentiometer. The power consumed by the armature was very small (about 10 watts at full speed) since all the rotating parts were mounted in ball bearings and the only sliding resistance was that due to the brushes.

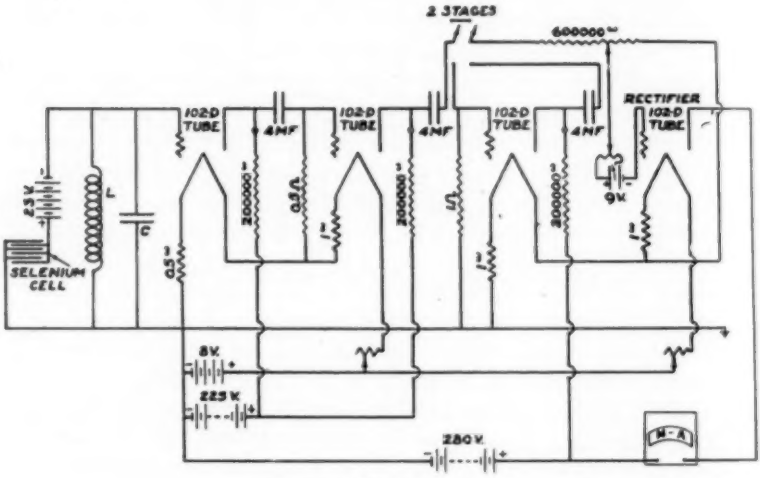


FIG. 6

A diagram of the electrical circuit which was used for selecting and measuring is shown in Fig. 6. The anti-resonant circuit, with a damping factor of 50 ohms per henry, depends as well upon the high internal impedance of the selenium cell for its selectivity. A potential amplification of about 13 000 is obtained by the three stages of amplification. When this output potential is too large for the rectifier a known fraction of it is tapped off by means of the potentiometer. The rectifier is calibrated for plate circuit current (micro-amperes) against input voltage. For a voltage less than 6, the plate current characteristic is very nearly parabolic, hence the rectifier greatly enhances the selectivity of the system. Although the overall selectivity of the system was considered

sufficient for the present use, it can be greatly increased by the addition of more anti-resonant circuits between the stages of the amplifier.

Two sets of reductions are necessary in order to obtain the spectrum from the observations made with the apparatus. First, the frequency of the measured component is determined by $f=f_a S/S_a$ where f_a is the tuning frequency of the circuit, S is the speed at which the original record was made, S_a the speed of the strip past the image of the slit. Second, the relative amplitude is to be derived from the amplifier output potential and the calibration of the apparatus. Two cases here arise: the frequency separation of the components of the generated wave may be large compared with the frequency range over which the tuned system gives appreciable response; or, as in the case of vowel sounds, the spectrum of the generated wave may be so dense that for the purpose of calculation it may be treated as a band spectrum.

In the former case, the output is divided by the maximum ordinate of the response curve. Such a condition obtains when the auxiliary calibrating wave is used. This wave consists of alternate opaque and transparent bands of equal width, and is far easier to make than a sine wave. The generated wave is then of the type shown in Fig. 3. The fundamental is thus available for calibrating the entire system for low frequency tuning while the first few harmonics are similarly useful for the higher frequencies.

In the second case, a first approximation is taken, since it would be impracticable to derive the exact values of the amplitudes. The output potential is multiplied by the area correction factor derived on the assumption that the spectrum is constant throughout the frequency range covered by the response of the tuned system. This approximation is closer, the greater the selectivity; furthermore it is closest when the speed is such that the tuning frequency coincides with a frequency at which the spectrum of the generated wave has a maximum or minimum. In this case, the factor is $S/(S_a\sqrt{A})$ where A is the area of the curve of rectifier output current per unit amplitude of harmonic variation in the generated wave, plotted against frequency of the variation. The speed ratio is here taken into account because it determines the density of the lines in the spectrum of the generated wave.

Since a knowledge of the maxima and minima is of great importance in determining the graph of any function, this apparatus is operated most advantageously by adjusting the speed for critical readings in the rectifier output. The ease of operation and reduction of observations is

also made much greater by the use of adjustable speed with but few widely separated tunings rather than a fixed speed with variable tuning. Undoubtedly more will be done in the future to develop this apparatus especially by the use of a photoelectric cell together with greater selectivity to increase the precision at high frequencies.

RESEARCH LABORATORIES OF THE
AMERICAN TELEPHONE AND TELEGRAPH COMPANY
AND THE WESTERN ELECTRIC COMPANY, INCORPORATED
MAY 6, 1924

A Direct Reading Pyrometer of the Disappearing Filament Type.—The disappearing filament type of optical pyrometer as ordinarily constructed labors under two disadvantages:

1. It is not practicable to attach a temperature scale directly to the ammeter as the lamps differ so much from one another that the replacement of a lamp would necessitate a new scale for the ammeter.

2. The lowest measurable temperature corresponds approximately to a current of one half the maximum value so unless some method of shifting the zero is employed, one half the ammeter scale is useless as far as temperature measurement is concerned.

The arrangement described by the authors eliminates this latter difficulty completely and also appears to be a practical solution of the first problem. The pyrometer lamp forms one arm of a Wheatstone Bridge which is so proportioned as to be balanced at the lowest readable temperature. The usual galvanometer is replaced by a suitable ammeter and series resistance, the current through the meter being of course zero at the temperature mentioned and increasing continuously with rise in temperature. The circuit can obviously be so proportioned as to make the ammeter range just correspond to the useful range of temperature and it is apparently also possible to compensate for variations from lamp to lamp by changing the otherwise fixed resistances in the Wheatstone Bridge.—[F. H. Schofield and D. C. Gare, Jour. of Sci. Inst., 1, pp. 193-198, 1924.]

L. BEHR

Spectrum of once-ionized Carbon.—Interpreting observations of his own in the commonly accessible regions of the spectrum and of Simeon's and Millikan's in the extreme ultraviolet, Fowler correlates the series of once-ionized carbon; they are doublet series, according to Sommerfeld's displacement law; the highest terms are the common limits of the diffuse and sharp series 196670 and 196612, giving 24.3 volts for the second ionizing potential of carbon. [A. Fowler; Nature, *113*, p. 446; 1924. Proc. Roy. Soc. *A105*, pp. 299-310; 1924.]

K. K. DARROW

METHODS OF MEASURING THERMAL CONDUCTIVITY IN SOLIDS AND LIQUIDS*

By L. R. Ingersoll

The coefficient of *thermal conductivity*, k, is (c.g.s.) the number of calories per sq. cm per sec., flowing under a temperature gradient of 1°C. per cm. With the exception of those listed under IV below, all the methods described involve a *steady state* (as regards time) of temperature in the body and yield the conductivity either directly or by a comparison process. Variable state methods give the *diffusivity* or "thermometric conductivity," $h^2 = k/cd$, from which the conductivity may be computed if the specific heat c and density d are known. While variable state methods are increasing in number, because in many cases of heat flow it is the diffusivity rather than the conductivity which directly controls conditions, by far the larger proportion of measurements involve the steady state. The modern tendency is toward greater directness than formerly. Lateral losses are avoided so far as possible by making the specimens shorter and wider, by guard rings, or in an increasing number of cases by use of the cylindrical or spherical methods. Mercury thermometers have been almost entirely displaced by thermoelements or, less frequently, by resistance thermometers, while electrical heating is extensively used and the heat flow calculated from the energy supplied.

For the best general account of heat conductivity measurements see Glazebrook, Dict. of Appl. Physics, *I*, p. 429, 1922; also Chwolson, Lehrb. d. Phys., *III*, p. 324; 1905; Winkelmann, Handb. d. Phys., *III*, p. 435; 1906; Kohlrausch, Prakt. Phys., p. 209; 1910. For description of most of the older methods the reader is referred to any of these.

I. *Linear Flow. Wall Method—Poor Conductors.* This is particularly suitable when the material is readily obtainable in the form of plates or slabs whose width is several times the thickness. It is seldom used for good conductors like metals, on account of the difficulty of measuring the temperature difference between the two faces sufficiently

* One of a series of reports prepared at the request of the Committee on Research Methods and Technique appointed by the Division of Physical Sciences of the National Research Council. It is the purpose of these reports to present in brief outline a summary, more or less critical, of the methods which may be employed in various kinds of Physical measurements. See Editorial in this Journal, *9*, p. 410, 1924.

accurately, although Hall[1] met this difficulty by coating both surfaces of his specimen (iron plate 10 cm diameter × 2 cm thick) with copper and attaching copper wires to each face, thus forming a differential copper-iron thermocouple.

Peirce[2] measured conductivity of slabs of rock (60 cm sq. × 10 cm thick) placed between steam and ice chambers. Temperatures of faces were determined with thermo-elements and heat flow through a definite central portion of slab determined from ice melted. Temperature drop in the specimen was reduced by placing it between two thin plates of similar material. Method suitable for large size specimens.

The National Physical Laboratory[3] (England) has developed apparatus for the rapid test of commercial wall insulators and similar materials by placing an electrically heated plate 3 ft. sq. between two similar slabs of the specimen under test, the outer faces being kept cold. Edge losses are eliminated by a guard ring 1 ft. wide, also electrically heated. See also Biquard.[4]

Griffiths[5] in using materials with rough surfaces (e.g. brick) secured a uniform temperature of the hot face by contact with molten metal (e.g. tin). The other face was water cooled and the heat outflow measured by a continuous flow calorimeter.

In the method developed by Griffiths and Kaye[6] the specimens were small (45 mm diam. × 0.5 to 4 mm thick) and arranged as in (3) on each side of an electrically heated copper disc, the outer surfaces being in contact with water cooled copper blocks. Thermo-elements in both inner and outer copper discs gave the temperature gradient. A guard ring was unnecessary. The method is fairly accurate—1 to 2%— and particularly adapted to porous materials tested under a definite pressure. Cf. Lees[7] who used specimen on only one side of heater.

Christiansen[8] developed a comparison method in which a plate of the specimen and one of a standard substance, e.g. glass, were placed together with thin copper sheets between and on each side. If a steady normal flow of heat was maintained through the plates the conductivities were inversely proportional to the two temperature gradients, as

[1] Proc. Am. Acad. *34*, p. 283; 1898.
[2] Proc. Am. Acad. *38*, p. 651; 1903.
[3] Annual Report, 1919.
[4] C. R., *150*, p. 268; 1910.
[5] Trans. Faraday Soc., *12*, p. 109; 1917.
[6] Proc. Roy. Soc., A, *104*, p. 71; 1923.
[7] Phil. Trans. A, *191*, p. 399; 1898.
[8] Wied. Ann., *14*, p. 23, 1881.

determined by thermo-elements embedded in the copper plates. Paalhorn[9] compared in this way the conductivities of glass and air. When used with guard ring, this method is applicable to very small specimens; see Sieg[10], also Van Dusen.[11]

II. *Linear Flow. Bar Method—Metals.* Gray[12] used specimens in form of bars 4 to 8 cm long and 2 to 4 mm diameter, protectively wrapped. The ends screwed into a copper hot-water bath, and 6 cm copper sphere which served as calorimeter. This is one of the simplest methods, lateral heat losses being largely eliminated. For a somewhat similar method applicable to small specimens under high pressure see Bridgman.[13]

Jaeger and Diesselhorst[14] made careful determinations of the ratio of thermal and electrical conductivity using the method of Kohlrausch.[15] A constant electric current was sent through the bar, whose ends were kept at the same constant temperature by connection with water baths. From measurements by thermo-elements of the temperature difference between the middle of the rod and two points equidistant on each side, and also of the potential difference between the two outer points, the (ratio of electrical and thermal) conductivity could be calculated. Though somewhat indirect this is one of the best methods. For its application at temperatures down to 20° abs. see Meissner.[16] A variation of this method is described by O'Day.[17]

Using some of the same principles, Worthing[18] determined the conductivity of tungsten, tantalum and carbon as lamp filaments, at temperatures around 2100°C. by measurements with an optical pyrometer of the temperature gradient near the cooling junction. See also Langmuir.[19]

Lees[20] worked with a number of pure metals and alloys in the form of rods 7 to 8 cm long and 6 mm diameter, inside a thick copper cylinder and connected with it at one end. Heat was supplied by coils at one end

[9] Diss. Jena, 1894.
[10] Phys. Rev., *6*, p. 213; 1915.
[11] J. O. S. A. & R. S. I., *6*, p. 739; 1922.
[12] Proc. Roy. Soc., A, *56*, p. 199; 1894.
[13] Proc. Am. Acad., *57*, p. 80; 1922.
[14] Abh. d. phys. tech. Reichsanstalt, *3*, p. 269; 1900.
[15] Ann. d. Phys., *1*, p. 145; 1900.
[16] Ann. d. Phys., *47*, p. 1001; 1915; Z. f. Physik, *2*, p. 373; 1920.
[17] Phys. Rev. *23*, p. 245; 1924.
[18] Phys. Rev., *4*, p. 535, 1914.
[19] Phys. Rev., *7*, p. 151; 1916.
[20] Phil. Trans. (A) 208, p. 381; 1908.

of the bar and on the outside of the cylinder and the conductivity was calculated from the difference of temperature gradients along rod under these two conditions of heating. The whole apparatus was contained in a Dewar flask and measurements were carried out down to liquid air temperatures.

Koenigsberger and Weiss[21] compared the conductivity of graphite, silicon, etc. with iron (cf. 8) by soldering or cementing bars about 3 cm long×4 mm diameter end-to-end and measuring temperatures with thermo-elements at known distances apart on each specimen while a constant flow of heat was maintained through the two in series. Then, if radiation and convection losses are small, the ratio of conductivity is the inverse ratio of the temperature gradient×sect. area. Accuracy estimated at 6 per cent with possibility of considerable improvement if bars are placed in evacuated chamber with reflecting walls. A simple method well adapted to measurements of both thermal and electrical conductivity for comparison purposes.

Brown[22] and others have developed apparatus for working with certain metals in both solid and molten states. See Honda and Simidu[23] for tests on carbon steels and nickel up to 900°C. For application of the bar method to very small specimens, as of the rare metals, see Barratt.[24]

III. *Radial Flow.* When the materials, particularly poor conductors, can be formed into cylinders or hollow spheres there are certain advantages in the radial flow method due to the partial or total elimination of lateral heat losses. The advantage gained in this way, however, is sometimes lost through difficulties in temperature measurement.

Niven[25] used specimens in the form of two half cylinders, 9 cm diam.×15 cm long, which fitted accurately together. A known amount of heat, Q,—per cm length, per sec.—was supplied by current in a platinoid wire along the axis, and the temperatures T_1 and T_2 were determined by thermo-elements at radial distances a and b (1 cm and 3 cm). Then from the relation $Q \log b/a = 2\pi K\ (T_1 - T_2)$ the conductivity could be computed. Poole[26] used this method for certain rocks up to 500°C. while Clement and Egy[27] tested fireclays in this way up to

[21] Ann. d. Phys., *35*, p. 1; 1911.
[22] Phys. Rev. *22*, p. 171; 1923.
[23] Tohoku, Univ. Sci. Reports, *6*, p. 219; 1917.
[24] Phys. Soc. Proc., *26*, p. 347; 1914.
[25] Proc. Roy. Soc., *76*, p. 34; 1905.
[26] Phil. Mag., *27*, p. 58; 1914.
[27] Met. and Chem. Eng., *8*, p. 414; 1910.

800°C. For application of the cylindrical method to wax, sand, etc. see Melmer.[28]

Angell,[29] using a method suggested by Mendenhall, heated nickel and aluminum rods 1.2 cm diam. ×15 cm long by a transformer current and determined temperatures by thermo-elements in an axial hole and at the surface. Thermo-element on surface was rolled very thin and protected by thin sheet of same metal as rod. Determinations were made up to 600°C. for Al and 1200°C. for Ni. The method is not applicable when "skin effect" is shown.

E. E. Hall[30] avoided the end losses of the cylindrical method in testing iron by using a hemispherical end cap as suggested by Hering.[31]

Laws, Bishop and McJunkin[32] measured the conductivity of cast iron, using a hollow sphere formed of two hemispheres—int. diam. 8 cm, ext. 15 cm—filled with (stirred) oil and immersed in a bath of oil. Q cal./sec. was supplied by resistance coil in the cavity and the temperature difference between outer and inner surfaces determined with thermo-elements formed by electroplating the surface with copper and using copper leads. (cf. 1). Then $k = \frac{Q\,(R_1 - R_2)}{4\pi(T_2 - T_1)R_1R_2}$. Bishop[33] measured the conductivity of lead in this way and made a careful study of the accuracy of the method which he estimated at 1 per cent or better. See also Peczalski.[34] Nusselt[35] tested asbestos and similar materials by packing them between two metal spherical shells of about 15 cm and 60 cm diam.

IV. *Variable State.* King[36] applied to a wire a periodic flow method resembling that of Angstrom.[37] A periodic source of heat was supplied at one end and the time lag of the deflection of the galvanometer connected with two thermo-elements a few cm apart on the wire allowed the diffusivity h^2 to be calculated. Tadokoro[38] used a similar method in measuring the diffusivity and conductivity of many materials such as

[28] Akad. Wiss. Wien., Sitz. Ber., *120*, p. 269; 1911.
[29] Phys. Rev., *33*, p. 421; 1911.
[30] Phys. Rev., *19*, p. 237; 1922.
[31] Trans. Am. Electrochem. Soc., *18*, p. 213; 1910.
[32] Am. Acad. Proc., *41*, p. 457; 1906.
[33] Am. Acad. Proc., *41*, p. 671; 1906.
[34] C. R., *160*, p. 766; 1915.
[35] Forsch. Ver. d. Ing., Hefte 63, 64; 1909.
[36] Phys. Rev., *6*, p. 437; 1915.
[37] Phil. Mag., *25*, p. 130; 1863.
[38] Tohoku Univ., Sci. Reports, *10*, p. 339; 1921.

bricks and cements. For measurements on snow see Okada, Abe and Yamada.[39]

Ingersoll and Zobel[40] made measurements on a porcelain plate in which one surface was suddenly heated to and kept at a constant temperature—perhaps 60°C.—while the temperature-time curve of the other surface, protectively wrapped, was determined, allowing the diffusivity to be calculated. Ingersoll and Koepp[41] applied this principle with success to a variety of sands, muds and clays packed in a flat copper box 8 cm wide and 18 cm deep and long. To make sure that the heat flow was normal to the flat faces the narrow sides were lined inside with paraffined wood. A flat resistance thermometer in the center connected with a graphical recorder gave the temperature and when, after standing for a day or two, this had reached a constant value, the box was place in stirred ice water. From the resultant temperature curve the diffusivity was readily calculated; from measurements of specific heat and density the conductivity was arrived at.

V. *Crystals.* In the original de Senarmont[42] method, a plate of the crystal was thinly coated with wax and heat applied at a point near the center. The resulting ellipses or circles melted in the wax allowed the relative conductivities in different directions to be measured. This method has been applied, with some modification, by Badior[43] in working with substances rendered artificially anisotropic by pressure. Voigt[44] also developed a method involving the use of isothermals in wax covered plates which could be used for metals (see Rietzsch[45]) as well as crystals.

Lees[46] compared the conductivity of crystals with brass by placing thin slices between brass bars and comparing the temperature gradients in the crystal and in the bar. Cf. method 8.

VI. *Steady State. Liquids.* Several of the methods already described are applicable to liquids, or even gases, if suitable precautions—heating from the top—are taken to prevent convection, but, in general, special apparatus has been developed. Jakob,[47] in measuring the conductivity of water, made use of a vacuum vessel to reduce error through losses. The heat electrically generated passed vertically down through

[39] Math. Phys. Soc., Tokyo, Proc., *4*, p. 385; 1908.
[40] Math. Theory of Heat Conduction, p. 116, Ginn.
[41] Phys. Rev.; July 1924.
[42] Ann. Chim. Phys., *21-23*; 1847-8.
[43] Ann. d. Phys., *31*, p. 737; 1910.
[44] Wied. Ann., *64*, p. 95; 1898.
[45] Ann. d. Phys., *3*, 416; 1900.
[46] Phil. Trans. (A) *183*, p. 481; 1892.
[47] Ann. d. Phys., *63*, p. 537; 1920.

the layer of liquid 11.7 cm diam. $\times$2 mm thick, between heavy copper plates with embedded thermocouples. Accuracy estimated at 1 per cent. See also Weber[48] (water, glycerine, mercury, petroleum, etc.); Hernquist[49] (hexane, etc.) Lees also applied method (7) to liquids. For an ingenious flow method see Nettleton,[50] and also Callendar.[51]

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Various Electrical Effects of Light upon Selenium and upon Cuprous Oxide.—Measurements were made upon the change in conductivity, by the usual method; upon the Becquerel effect, by connecting a galvanometer across a cell consisting of water or very dilute nitric acid in which an electrode of the substance was dipped (the other electrode being of the same substance or of a metal) and observing the galvanometer deflection (later calibrated with a potentiometer) when the first electrode was irradiated; and upon the threshold wave length of the photoelectric effect. This last was determined by the unusual device of putting screens of glass in the path of the undispersed light beam (from an Al spark or Fe arc) and subsequently measuring the transmission curve for the thickest screen which just let through light enough to produce a detectable effect. The thresholds were located at 2260A for Se and 2572A for Cu_2O. The other measurements were made with dispersed light, of which the intensity was measured with a thermocouple. The curves of Becquerel effect and resistance—change vs. wave length all show maxima in the experimental range (5000 to 9000A) but the exact result depends on the method chosen to reduce the data for different wave lengths to equivalent intensities, since the effects are usually not always proportional to the first power of the intensity.—[V. P. Barton, Johns Hopkins; Phys. Rev. *23*, pp. 337-344; 1924.]

K. K. DARROW

Interpretation of the Infrared Absorption Bands of HCl, HBr and HF.—These bands are interpreted according to the theory of Born and Hückel, who have worked out an expression for the total energy (vibrational+rotational) of a molecule consisting of two atoms, normally at a distance r_0 from one another, and subject to a restoring-force $f=ar+br^2+cr^3$ when this distance is changed from r_0 to r_0+r. Absorption of energy by the molecule results in changing the angular momentum integral of the molecule by one quantum, and simultaneously changing the radial momentum integral from nh to

[48] Ann. d. Phys., *11*, p. 1047; 1903.
[49] Ark. f. Math. Ast. Fysik, Stockholm, *8*, p. 1; 1913.
[50] Phys. Soc. Proc., *25*, p. 28; 1913.
[51] Phil. Trans., (A), *199*, p. 110; 1902.

n_0h, where $n > n_0$. The experimental material for HCl consists of measurements on three bands, corresponding respectively to $n=1$, $n_0=0$; $n=2$, $n_0=0$; $n=2$, $n_0=1$. Most of the data relate to the first two bands, the "fundamental" and its "overtone"; in each, the frequencies of the lines are represented by four-constant formulae, $A+Bm+Cm^2+Dm^3$, when successive integer values are given to m. This is the sort of formula to be expected from the Born-Hückel model, and the coefficients A, B, C, D are expressible in terms of r_0, a, b, c and the masses of the atoms. The coefficient D ought to be the same for both bands, but is not. Otherwise the cross-relations between the two sets of values for A, B, C, are compatible with theory, and make it possible to calculate r_0, a, b, and c. The equilibrium distance r_0 comes out 1.27A for HCl (for HBr 1.37A and for HF 0.97A, but the data are to be regarded as less reliable). The restoring force is very unsymmetrical; an inward displacement of the atoms is resisted by a much greater force than an outward one. Applying the radial quantum condition, the amplitude of oscillation may be calculated; measured from one end of the path to the other, it is 0.246A for the one-quantum vibration and 0.358 for the two-quantum one. It follows that the H atom must lie between the second and third electron shells of the Cl atom. [H. Bell, Manchester; Phil. Mag. *47*, pp. 549-560; 1924.]

K. K. DARROW

Electrostatic Fields of Grids and Diaphragms.—Semenoff has pointed out that the published results on ionization potentials may be in error due to an incomplete knowledge of the actual distribution of potential. It is customary to assume that the electrons passing through the grid have had their energy increased by an amount proportional to the potential difference between the grid and the emitting electrode. In general this assumption is not correct, the energy increase is smaller. The electrostatic field in the neighborhood of grids and diaphragms is investigated by the method cited above and the conclusion arrived at, that with grids of the usual proportions an error of one per cent is possible but that the error for diaphragms can readily be reduced to a negligible value.

Walther and Inge, ZS. f. Physik *19*, pp. 192-205, 1923.

L. BEHR

Continuous Spectrum of Hydrogen.—Several observations on this, the spectrum of the familiar "blue glow," have recently been published. Horton and Davies, referring to their own publication on the subject, express the opinion that it is produced when electrons of energy exceeding 12.6 volts and inferior to 15.9 volts strike and dissociate hydrogen molecules; the light is supposed to be emitted when the atoms recombine.—[F. Horton and A. C. Davies: Nature, *113*, pp. 273-274; 1924.]

K. K. DARROW